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December 22, 2011

Mr. Tien Q. Duong
EE-2G/Forrestal Building
Office of Vehicle Technologies
U.S. Department of Energy
1000 Independence Ave., S.W.
Washington D.C. 20585

Dear Tien,

Here is the fourth-quarter FY 2011 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://batt.lbl.gov/reports/quarterly-reports/>.

Sincerely,

Venkat Srinivasan
Acting Head
BATT Program

edited by: V. Battaglia
M. Foure
S. Lauer

cc:	J. Barnes	DOE/OVT
	P. Davis	DOE/OVT
	D. Howell	DOE/OVT
	J. Muhlestein	DOE-BSO

FEATURED HIGHLIGHTS

Cell Analysis–

- ✚ Chen's Group confirms the correlation between ordering and increased Ni content in $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ -spinel materials.

Anodes–

- ✚ Kumta's Group deposits amorphous Si electrode that cycles well at 1300 mAh/g.

Electrolytes–

- ✚ Goodenough's group identified an optimum composition of an oxide with a garnet framework for Li conduction.

Diagnostics–

- ✚ Grey's Group uses NMR to develop an atomistic mechanism for the charging of Si with Li.

Modeling–

- ✚ Newman's Group measure impedance of HOPG on different facets before and after the formation of the SEI and shows the impedance is worse on the basal edge where Li insertion occurs.
- ✚ Srinivasan's Group measures the diffusion coefficient of Li in NCM as a function of SOC, and explains the why the material is fast charging.

BATT TASK 1 **CELL ANALYSIS**

TASK 1.1 - PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Electrode Fabrication and Failure Analysis

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy systems: low energy; poor cycle life; poor calendar life

OBJECTIVES: 1) Provide electrodes, cells, and/or cycled cell components to BATT researchers. Bring fundamental understanding to electrode construction. Provide a comprehensive, independent assessment of promising materials designed to meet high-energy performance and cycling requirements, and allow for the differentiation between material failures and electrode/cell failures. 2) Determine some of the source/s and/or cause/s of cell failure.

GENERAL APPROACH: Objective 1) accomplished through methodically changing different aspects of the electrode fabrication process and examining the result of the changes *via* electrochemical and physical and chemical characterization techniques. Objective 2) accomplished, primarily, through electrochemical characterization of electrodes against different counter electrodes and then performing *ex situ* physical characterization studies, such as EDX, ICP, SEM, and TEM.

STATUS OCT. 1, 2010: There appears to be a correlation between Young's modulus and cycle life for cells with PVdF - the smaller the Young's modulus the longer the life. Full cells self discharge; VC modifies the self discharge of a full cell but does not affect the self discharge of graphite in half cells. The oxidation of the electrolyte has three regimes: <4.3 V; 4.3 V <> 4.6 V; > 4.6V. Binder systems containing SBR result in less 1st cycle irreversible capacity loss but do poorly at protecting the anode during long-term cycling.

STATUS SEP. 30, 2011: Good electrodes of LiNi_{1/2}Mn_{3/2}O₄ will have been distributed to BATT PIs. The solubility of different Mn compounds will have been measured. The rate of side reaction on both electrodes in a Graphite/NCM cell will be known. The dissolution of a high-voltage cathode will be known.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l; 5000 deep-discharge cycles; 15 years.

MILESTONES:

- (a) Procure 20 g of a good source of LiNi_{1/2}Mn_{3/2}O₄. (Jan. 11) **Complete**
- (b) Supply laminates of LiNi_{1/2}Mn_{3/2}O₄ that cycle 100 cycles. (Apr. 11) **Complete**
- (c) Report the solubility of Mn compounds. (Apr. 11) **Complete**
- (d) Report the rate of side reaction of NCM *vs.* Li and *vs.* Graphite. (Jul. 11) **Complete**
- (e) Report the rate of side reaction of LiNi_{1/2}Mn_{3/2}O₄ *vs.* Li. (Sep. 11) **Complete**

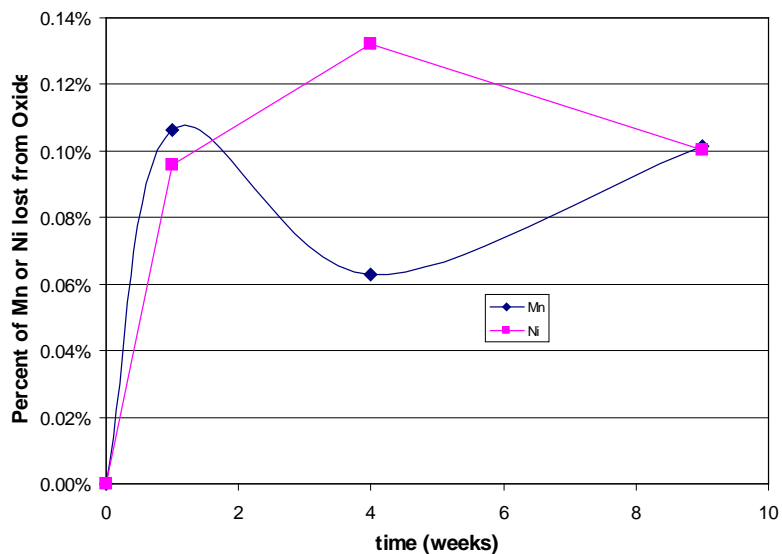
PROGRESS TOWARD MILESTONES

(a) Procure 20 g of a good source of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. (Jan. 11) **Complete**.
See 1st Quarterly Report.

(b) Supply laminates of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ that cycle 100 cycles. (Apr. 11) **Complete**. See 2nd Quarterly Report.

(c) Report the solubility of Mn compounds. (Apr. 11) **Complete**.

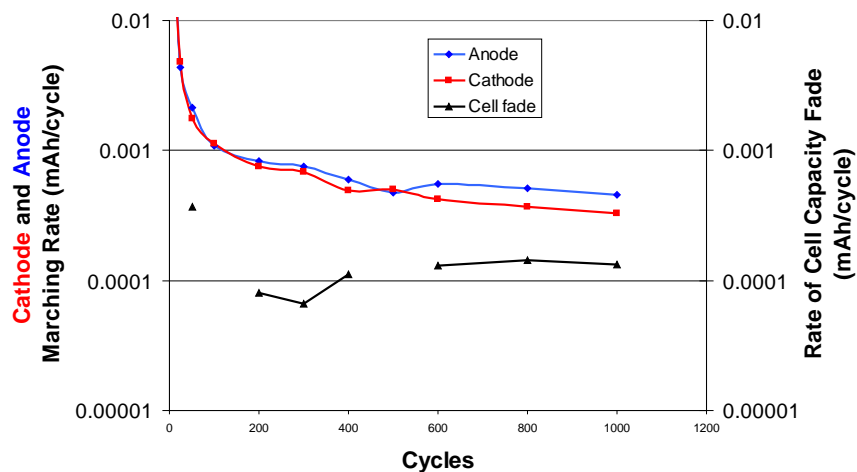
As explained in the previous quarter, the dissolution experiments needed to be repeated due to some equipment malfunctions. For this round, we measured the rate of dissolution of Ni and Mn from fresh electrodes of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ (NEI). Electrodes of approximately 100 mg of active material were added to 12 g of electrolyte in leak proof Teflon bottles and held at 55°C for 9 weeks. Samples were taken at 1, 4, and 9 weeks and measured for Ni and Mn content with an ICP-OES. The graph to the right shows that approximately 0.01 % of both Ni and Mn are lost from the spinel within the first week and then holds steady for the next 9 weeks. We found very similar results for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. We plan to repeat this experiment for electrodes at different states of charge.



(d) Report the rate of side reaction of NCM vs. Li and vs. Graphite. (Jul. 11) **Complete**.
See 1st Quarterly Report.

(e) Report the rate of side reaction of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ vs. Li. (Sep. 11) **Complete**.

We completed the measurements of Ni-spinel side reactions vs. Li and vs. graphite. The results in the figure show the rate at which the anode and cathode are sliding as a result of the net effect of side reactions and impedance rise in each electrode. The difference in the rates at which the electrodes are moving relative to each other gives the capacity fade of the cell. This cell cycled



1000 cycles and lost *ca.* 20% of its capacity over that time. As can be interpreted from the figure, the rate of the side reaction at each electrode is slowing down at the same rate leading to a constant rate of capacity fade of the cell. The side reactions at the cathode and anode are approximately 4 and 5 times faster, respectively, than the rate of the capacity fade of the cell.

TASK 1.2 - PI, INSTITUTION: Thomas Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – High-energy Density Cathodes and Anodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000cycles/58 MWh).

OBJECTIVES: Synthesize and evaluate new electrode materials with improved energy density. Investigate the relationship of structure, morphology and performance of cathode and anode materials. Explore kinetic barriers, and utilize the knowledge gained to design and develop electrodes with improved energy density, rate performance and stability.

GENERAL APPROACH: Identify candidate electrode compositions by systematic analysis of phase diagrams and literature reports. Synthesize novel materials and/or unique structures and employ XRD, electron microscopy, vibrational spectroscopies, and electroanalytical techniques to determine their applicability to BATT goals. Characterize known and modified electrode materials and establish correlations between crystal structure, morphology and performance. Provide guidelines for materials synthesis and electrode fabrication processes.

STATUS OCT 1, 2010: It was shown that prelithiated silicon and tin powders have greatly reduced first-cycle capacity losses and exhibit superior cycling stability to elemental Si and Sn powders. Similar synthetic procedures can also be used to partially or fully prelithiate carbon anodes. The high reactivity of the prelithiated materials mandates use of non-oxidizing binders and solvents. Several alternative cathode materials containing cobalt and copper were prepared by ion exchange and by direct solid-state synthesis. Their electrochemical properties were disappointing, however, and work on these materials was concluded. A new technique for visualizing charge distribution in Li battery electrodes was developed in collaboration with staff at the Advanced Light Source and applied to cathodes in cross section and in the current collector plane.

STATUS SEP. 30, 2011: A new set of novel 4 V class cathode materials with capacities exceeding 200 mAh/g will be synthesized and their potential utility evaluated. Appropriate binder/solvent combinations will be identified for use with prelithiated intermetallic anodes. Charge distribution diagnostics will be applied to electrodes harvested from commercial cells.

RELEVANT USABC GOALS: 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

MILESTONES:

- (a) Report results of current and charge distribution assessments of harvested cathodes. (Feb. 11) **Complete**
- (b) Report on capacity retention in Si-based alloys with reduced irreversible capacity. (Mar. 11) **Canceled due to change in research direction to diagnostics.**
- (c) Report capacities and charge-discharge potentials for new cathode materials. (Jun. 11) **Canceled due to change in research direction to diagnostics.**

TASK 1.3 - PI, INSTITUTION: Karim Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Analysis – Interfacial Processes: SEI Formation and Stability on Cycling

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy and poor cycle/calendar life

OBJECTIVES: Synthesis and evaluation of high voltage cathode (spinel Mn-Ni) with improved electrochemical stability. Reduce the oxidation of the cathode composition, electrolyte, and separator. Find the appropriate alternative anode material composition that meets the requirement for low cost and high energy. We will continue the development of binders for the cathode and alternative anode to understand and improve the properties of the SEI layer.

APPROACH: Our approach is to develop an appropriate method to stabilize the interface reaction of the high-voltage oxide (Mn-Ni based, *e.g.*, LiMn_{1.5}Ni_{0.5}O₄) cathode by surface coating with a more stable material such as an olivine. The emphasis is to improve electrochemical performance at high voltage. The effect of the type of binder, electrolyte composition, and separator on performance at high voltage will be investigated. Our research on high capacity anodes will focus on Si-based compositions that will be optimized by varying the graphite and SiO_x content.

STATUS OCT. 1, 2010: Due to the decision by the BATT Program, we redirected our project to investigate Si-based anode alloys, LiMn_{1.5}Ni_{0.5}O₄ cathode, and stability of the SEI. This effort started in August 2010 by exploring an appropriate composition of anode material based on carbon-coated nano-silicon, SiO_x and graphite. Work on the high-voltage cathode by reducing its oxidation reactivity with the electrolyte was addressed.

STATUS SEP. 30, 2011: Due to its low cost and high capacity, the development of silicon-oxide anodes will continue to achieve the DOE objectives, and research will be conducted to find a suitable composition of the Si-based high capacity anode. Different anode composition; pure Si and its mixture with SiO_x and graphite will be investigated. For the cathode, high-voltage cathodes based on Mn-Ni spinel oxide will be used in this work. In order to reduce the oxidation of the electrolyte at high voltage, more stable binders, different electrolyte composition, carbon additives and surface coating of the cathode will be considered. In addition, investigation of the SEI layer on the anode and cathode, in particular the role of the binder type, electrolyte composition, and the cathode and anode composition will continue.

RELEVANT USABC GOALS: High energy and low cost: 96 Wh/kg (PHEV, 40 miles). Cycle life, calendar life: 15 year life (at 40°C).

MILESTONES:

- (a) Optimize a silicon-based composition as anode material. (Feb. 11) **Complete**
- (b) Demonstrate the benefit of surface coating of high-voltage LiMn_{1.5}Ni_{0.5}O₄ cathode with LiFePO₄ olivine material. (Sep. 11) **Complete**
- (c) Complete study of the effect of the binder type and electrolyte on the SEI layer by *ex situ* and *in situ* SEM analysis. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

The Si-based anode materials have many challenging aspects; *in situ* and *ex situ* SEM studies could provide a better understanding of their failure modes as they relate to capacity fade. In this quarter, we continued the characterization of this anode through the use of *ex situ* SEM. A number of Li/SiO_x-Graphite (1:1) cells with EC-DEC-1M LiPF₆ were discharged to different states: 0.5, 0.1, 0.05, and 0.005V, and charged to 2.5V. The electrodes from these cells were analyzed by SEM and compared to an uncycled electrode. The cross section of these electrodes is shown in Fig. 1; the baseline electrode shows (Fig. 1a) good porosity to absorb the volume expansion of the anode during cycling; however, this porosity is completely changed after the cell is *fully* discharged (5mV). The volume expansion caused densification of the electrode (Fig. 1c) and bigger particles were beginning to show cracks. The elemental chemical analysis of the discharged electrode shows a significant increase in the O content (most probably from Li₂O formation), particularly in the open porosity/binder region (Fig. 1b). When the cell is charged to 2.5V, a decrease in the O content compared to a fully discharged cell was observed, but still higher than the baseline electrode. This indicates the presence of an irreversible transformation. Also, the electrode reverts back to a porous state on charge to 2.5 V after the densification of the electrode when discharged to 5mV.

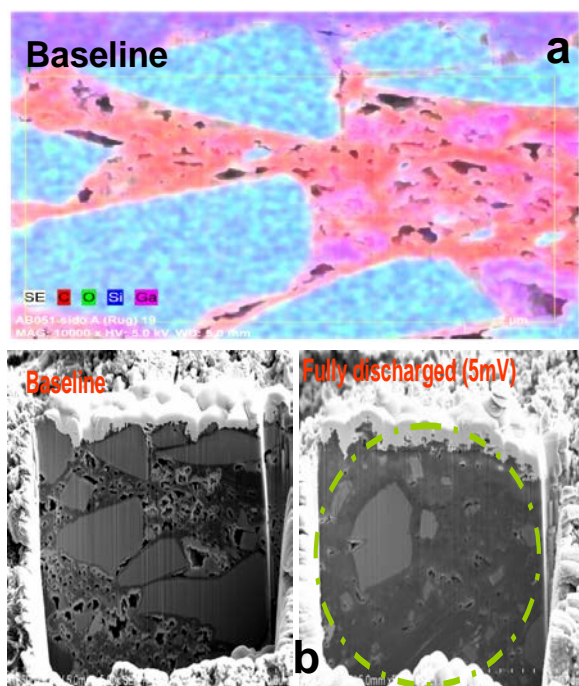


Figure 1. Reference electrode of SiO:Gr and fully discharged (5mV) in EC-DEC-1MLiPF₆.

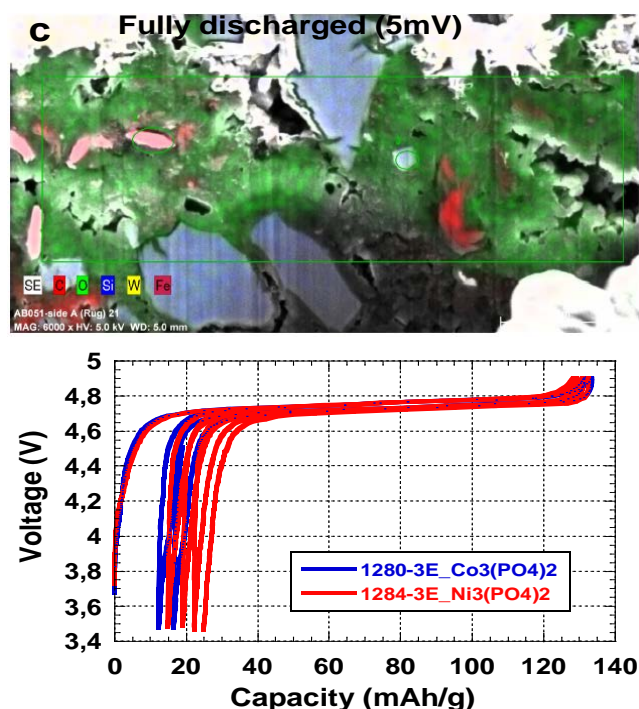


Figure 2. First few cycles of LiMn_{1.5}Ni_{0.5}O₄ coated with Co and Ni phosphate cathodes in Li/EC-DEC-LiPF₆.

Investigations of the high-voltage-spinel cathode material (LiMn_{1.5}Ni_{0.5}O₄) with a surface coating continued. The spinel material was coated with Ni and Co phosphate using a co-precipitation method. The first few cycles between 3.5 and 4.9 V at C/5 in standard electrolyte EC-DEC-1M LiPF₆ are shown in Fig. 2. The reversible capacities are 117 and 110 mAh/g for the electrodes coated with Co₃(PO₄)₂ and Ni₃(PO₄)₂, respectively. The first/second coulombic efficiencies are 90.7/96.5 and 88.4/96.4, respectively. The best performance was obtained with the Co₃(PO₄)₂ coating.

HQ is continuing its collaboration with members in the BATT program: Electrodes coated with Conoco Phillips graphite by HQ were sent to Vince Battaglia, and LiFPO₄ samples for *in situ* Raman were sent to Robert Kostecki.

TASK 1.4 - PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

TASK TITLE – PROJECT: Cell Analysis – New Electrode Design for Ultrahigh Energy Density

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy system: low energy, poor cycle life

OBJECTIVES: Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology for a range of electrode-active materials.

GENERAL APPROACH: Develop fabrication methods for high density sintered cathodes and anodes with controlled pore volume fraction and pore topology. Electrochemically test electrodes in laboratory half-cells and small lithium ion cells (<100 mAh), and model electrode response. Aim to increase cell-level specific energy and energy density by maximizing electrode density and thickness, under operating conditions commensurate with USABC targets for PHEV and EV.

STATUS OCT. 1, 2010: First fabrication and test results from directionally freeze-cast and sintered LiCoO₂ electrodes were reported.

STATUS SEP. 30, 2011: 1) Fabrication and testing of at least two cathode materials in the proposed high density electrode approach; 2) Complete 2-3 experimental cycles of electrode fabrication by the directional freeze-casting approach, sintering, and electrochemical testing to establish capacity vs. C-rate behavior for at least one of the targeted cathode compounds.

RELEVANT USABC GOALS: EV: 200 Wh/kg; 1000 cycles (80% DoD).

MILESTONES:

(a) Report fabrication procedure, structural characterization, and initial electrochemical test data for directional freeze-cast and sintered LiCoO₂ electrodes in laboratory scale lithium half-cells. (Mar. 11)**Complete**

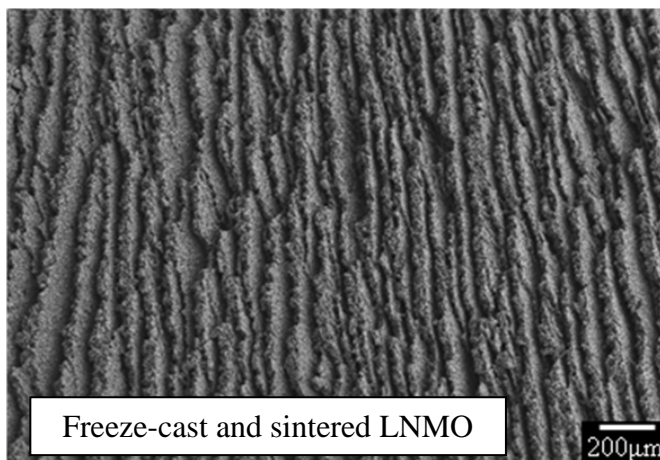
(b) Report results of sintering process development study for high-density additive-free LiNi_{0.5}Mn_{1.5}O₄ electrodes. (Jun. 11)**Complete**

(c) Report electrochemical test data for high-density additive-free LiNi_{0.5}Mn_{1.5}O₄ cathodes in laboratory scale lithium half-cells. (Sep. 11)**Complete**

PROGRESS TOWARD MILESTONES

Collaborator: Antoni P. Tomsia (LBNL)

Accomplishments: During the current reporting period, high-density, additive-free $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes prepared by sintering were electrochemically tested in Li half-cells. The first low-tortuosity electrodes of this material, produced by directional freeze casting, were also prepared. Concurrently, transport measurements were performed on sintered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as part of the activities under the new BATT Focus Group on High Voltage Ni-Mn Spinel (this latter work was not originally included under the 2011 AOP). These two sets of experiments have each informed the other and led to a self-consistent understanding of the rate-limiting step in electrochemical cycling of the high-density sintered electrodes.



The electronic conductivity of undoped $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was measured in its as-fired condition, for firing temperatures between 735 and 950°C. Consistent with trends shown by Kunduraci and Amatucci (*J. Electrochem. Soc.*, **153**[7] A1345 (2006)) it was observed that conductivity increases with increasing firing temperature at a constant oxygen activity (air). This can be understood as an increase in oxygen nonstoichiometry accommodated by the formation of Mn^{3+} . Upon electrochemical delithiation, however, it is expected that the Mn^{3+} is the first transition metal to be oxidized, and furthermore, being low in total concentration compared to the Li deficiency, is not the main determinant of electronic conductivity.

The conductivity vs. Li content x was then measured using DC current-interrupt measurements of half-cells, the changes in resistance being confirmed by EIS measurements to correspond to changes in the charge-transfer resistance rather than current collector or electrolyte resistance. The changes in the charge-transfer arc are attributed to changes in electronic conductivity. The interpretation of electronic conductivity in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is further complicated by the existence of three different cubic spinel phases varying in amount with x , as well as changes in cation ordering. The heat treatments applied were designed to obtain the cation-disordered state. From multiple measurements, in general, it was observed that the electronic conductivity has its maximum value at an intermediate SOC, with conductivities at $x \text{ ca. } 0.5$ being in the range of 2×10^{-4} S/cm to 1×10^{-3} S/cm. At both high and low SOC ($x \sim 0$ and $x \sim 1$), the conductivity is lower, being 2×10^{-5} to 1×10^{-4} S/cm. A hysteresis between charge and discharge was also observed; the cause of which remains to be understood.

Based on these values of electronic conductivity, the thickness of the sintered electrodes at which electronic conductivity will become rate-limiting can be estimated. For example, for a conductivity of 10^{-4} S/cm, an electrode of 250 μm thickness, cycling at a C/10 rate, produces a 0.3 V polarization due to the electronic resistance. Correspondingly, in multiple samples, it was observed that sintered, undoped $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, as currently prepared, is a low rate electrode exhibiting discharge capacities of *ca.* 100 mAh/g at a C/40 rate. Of interest in the next phase of this work are doping and other methods for increasing the electronic conductivity.

TASK 1.5 - PI, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – Advanced Binder for Electrode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy system: poor cycle life, high first cycle irreversible capacity, low coulomb efficiency.

OBJECTIVES: Develop new conductive polymer binder materials to enable large volume change lithium storage materials to be used in lithium-ion electrode.

GENERAL APPROACH: Use functional polymer design and synthesis to develop new conductive polymers with proper electronic properties, strong adhesion and improved flexibility to provide electric pathways in the electrode, and to accommodate large volume/phase change of the active material during lithium insertion and removal.

STATUS OCT. 1, 2010: Gained fundamental understanding of the functions of the conductive polymer in the Si electrodes; assessed the pros and cons of the different methods to compensate for first cycle loss of the Si/conductive polymer electrodes; and demonstrate full cell cycling capability of the Si/conductive polymer negative electrode.

STATUS SEP. 30, 2011: Investigate conductive binder properties to Si electrode performance in various electrode compositions and configurations; explore binder functionalities to increase coulomb efficiency; and explore the conductive binders in other high capacity material systems.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:

(a) Study conductive binder properties to Si electrode performance in various electrode compositions and configurations, aim to achieve 3.5 mAh/cm² loading electrode.(Mar. 11)

Complete

(b) Introduce binder functionalities to stabilized Si surface, minimize side reactions, and increase coulomb efficiency, aim to increase cycling efficiency from current 99 to 99.5%. (Sep. 11)

Complete

(c) Investigate the effectiveness of the conductive binders in other high capacity material systems. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

It has been demonstrated that the polymer binder is mobile in Si-based alloy electrodes. The volume change of Si during charge and discharge pushes around the polymer binder in the electrode, which in turn, gradually seals off the pores and reduces the area specific capacity. A process to improve the stability of the electrode was developed to limit the mobility of the polymers. Different loadings of electrodes from 0.4 to 3.7 mAh/cm² were produced based on this process. The cycling performance is reported in Fig. 1 with both area (a) and gravimetric (b) specific capacity. The initial gravimetric specific capacities are above 2000 mAh/g in all loadings. The capacity retention is very good up to 1.5 mAh/cm². The area specific capacity of 3.7 mAh/cm² is achieved. The electrode capacity retention behaves very differently from the conventional Si electrode at higher loadings: the capacity goes up in the first few cycles before fading.

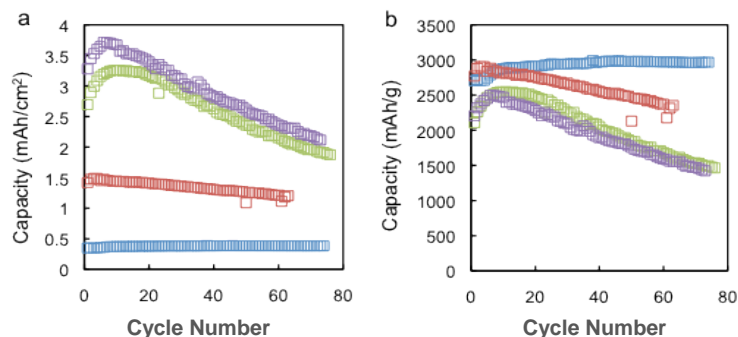


Figure 1. The cycling performance of Si nanoparticle and conductive polymer binder composite electrodes at different loadings. Each loading is color coded in a and b.

The coulombic efficiency (CE) of the conductive polymer and Si composite electrode improves during cycling as shown in Fig. 2. Three regions can be identified in the CE curve: the low CE region (95 to 99%) during the initial 200 cycles, the improved CE region (99 to 99.5%) from 200 to 500 cycles, and the stabilized CE region (99.5%) beyond 500 cycles. At the stabilized CE region, the specific capacity is still over 1800 mAh/g.

The conductive binder is also applicable to a Sn-nanoparticle-based electrode. Figure 3 demonstrates the initial cycling performance of this binder in combination with 100 nm, commercially-available, Sn nanoparticles. The reversible capacity is *ca.* 600 mAh/(gm of Sn).

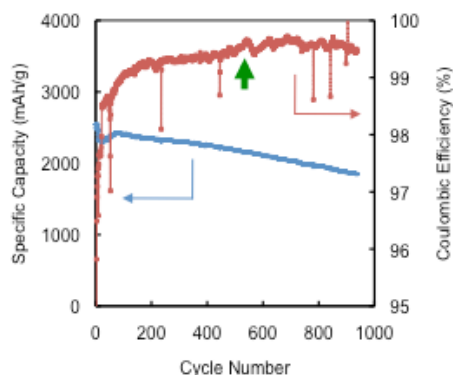


Figure 2. Long-term cycling performance and coulombic efficiency.

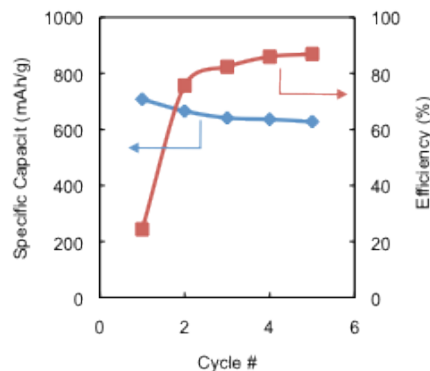


Figure 3. Initial cycling performance of conductive polymer in a Sn composite electrode.

Publications:

1. S. Xun; X. Song; Lei Wang; M. E. Grass; Z. Liu; V. S. Battaglia; G. Liu., The Effects of Native Oxide Surface Layer on the Electrochemical Performance of Si Nanoparticle-Based Electrodes. *J. Electrochem. Soc.*, to appear.
2. Gao Liu; Shidi Xun; Nenad Vukmirovic; Xiangyun Song; Paul Olalde-Velasco; Honghe Zheng; Vince S. Battaglia; Linwang Wang; Wanli Yang, Polymers with Tailored Electronic Structure for High Capacity Lithium Battery Electrodes. *Adv. Mater.*, appear online 2011.

TASK 1.6 - PI, INSTITUTION: Guoying Chen, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – High-Energy Density Cathodes: Improving Performance, Safety, and Cycle Life through Crystal Structure and Particle Morphology Design

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000cycles/58 MWh).

OBJECTIVES: Explore phase-transition mechanisms and kinetic barriers of high-voltage and high-capacity cathode materials. Establish direct correlations between crystal structure, composition, morphology, performance and stability. Provide guidelines to design and fabricate cathode materials with improved energy density, rate capability, and safety, especially with regard to thermal stability.

GENERAL APPROACH: Prepare well-formed crystals with various structure, composition, size and morphology using wet synthesis routes, such as solvothermal and molten-salt methods. Characterize their physical properties and investigate their solid-state chemistry using advanced spectroscopic, spectromicroscopic, scanning calorimetry, and electron microscopic techniques.

STATUS OCT. 1, 2010: Magnesium substitution in LiMnPO₄ was found to improve kinetics, structural, and thermal stabilities of the phosphate. Micron-sized LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC333) crystals with stoichiometric and excess amounts of Li were prepared by a molten-salt method. While the overlithiated oxide was well ordered with $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ super cells, the “Li-stoichiometric” sample lacks the same in-plane ordering in the structure. Chemical delithiation dissipates the cation ordering and disintegrates the overlithiated crystals, even at relatively low oxidation states with negligible volume change. Transformation from O3 to P3 structure occurred in both samples, but at a much higher oxidation state in the overlithiated sample.

STATUS SEPT. 30, 2011: Mixed transition-metal-phosphate crystals will have been prepared and evaluated for their kinetic performance and thermal stability. Layered oxide crystals with various Li, Ni, Co and Mn ratios will have been prepared. Structure analysis and property evaluation will have been performed on these crystals. Micron-sized Ni-Mn spinel crystals will have been synthesized.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD)

MILESTONES:

- (a) Report the synthesis of layered oxide crystals with various compositions. (Mar. 11) **Complete**
- (b) Report the phase transformation and thermal behavior of LiMMnPO₄ (M = Mg, Fe, Co and Ni). (Jun. 11) **Canceled due to change in research direction to concentrate on Ni/Mn spinels.**
- (c) Report structure and property evaluation of the layered oxide crystals. (Aug. 11) **Delayed to Feb. 12 due to change in project course.**
- (d) Report the synthesis of LiNi_{0.5-x}Mn_{1.5+x}O₄ crystals. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Ni/Mn Spinel: In collaboration with the BATT Ni/Mn Spinel Focus Group, work was initiated to investigate the effect of Mn^{3+} content on rate performance and stability of this high-voltage cathode. $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($0.3 \leq x \leq 0.5$) single crystals were prepared by the molten salt method, with the ratio between the Mn and Ni precursors carefully controlled to achieve the targeted stoichiometry. The crystals adapted the same octahedron shape and similar size of 2 μm . XRD patterns and lattice dimensions are compared in Fig. 1. The ionic radii of octahedral-coordinated Ni^{2+} , Mn^{3+} , and Mn^{4+} are 0.83, 0.785, and 0.67, respectively. Decreasing Ni^{2+} content increases the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and therefore leads to a slight expansion in the cubic lattice, Fig. 1b.

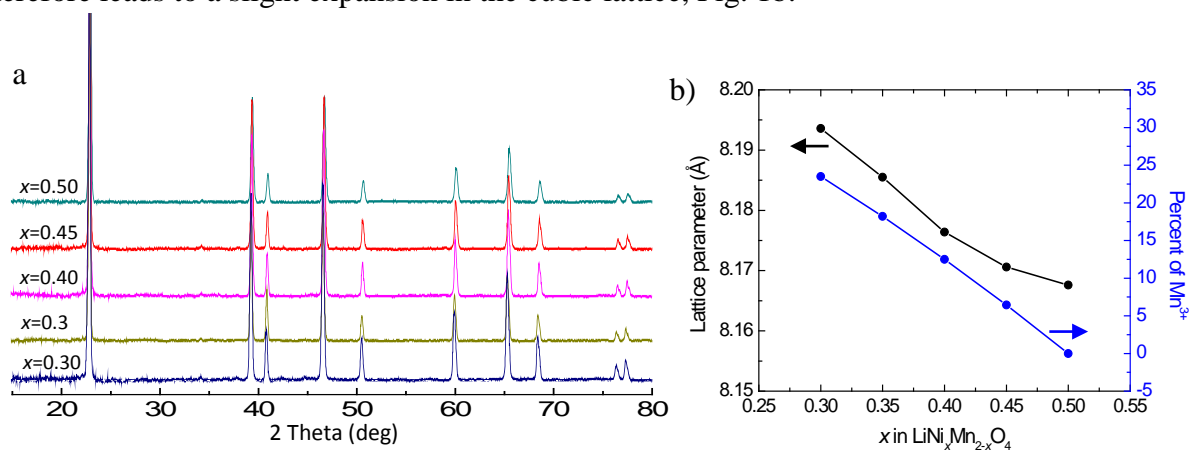


Figure 1. a) XRD patterns and b) lattice parameter and Mn^{3+} content in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($0.3 \leq x \leq 0.5$) crystals.

Figure 2a compares the FTIR spectra of the crystal samples. Bands at 620 and 560 cm^{-1} are attributed to Mn-O vibrations while the band at 590 to that of Ni-O. The replacement of Ni^{2+} by the smaller-sized Mn^{3+} leads to stronger Ni-O bonds and therefore a blue shift of the 590 peak at lower Ni content. The peak ratio of 590/620, which is commonly used as a qualitative measure of the transition-metal ordering in the structure, increased nearly linearly with Ni content (Fig. 2b). Peaks at 430, 560, and 650 are clearly present when Ni content is above 0.40, characteristic of an ordered crystal structure. Significant changes occurred on the spectrum when x decreased to 0.35, suggesting loss of the ordering. This report completes the work toward milestone (d) in FY2011.

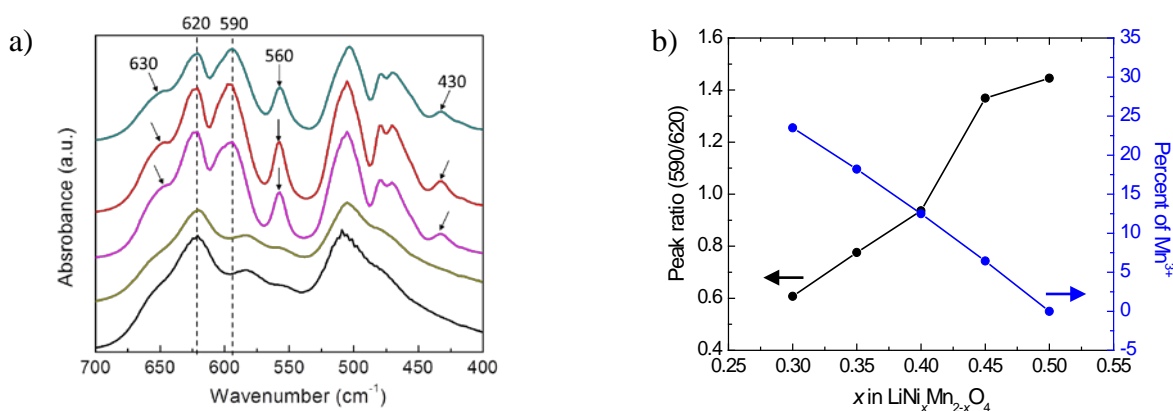


Figure 2. a) FTIR spectra and b) peak ratio of 590/620 and Mn^{3+} content in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ ($0.3 \leq x \leq 0.5$) crystals.

Collaborations this quarter: Richardson, Cabana, Grey, Kostecki, Doeff, SSRL, NCEM.

BATT TASK 2

ANODES

Task 2.1 - PI, INSTITUTION: Jack Vaughey, Michael Thackeray, Argonne National Laboratory

TASK TITLE – PROJECT: Anodes – Novel Anode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor low-temperature operation, and abuse tolerance limitations

OBJECTIVES: To address and overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes by designing electrode architectures containing main group metal, metalloid or intermetallic components that can tolerate the volumetric expansion of the materials and provide an acceptable cycle life.

GENERAL APPROACH: Our approach is to search for inexpensive anode materials that provide an electrochemical potential at least a few hundred mV above the potential of metallic Li. The focus will be predominantly on Sn- and Si-based systems. A major thrust will be to design new electrode architectures in which an electrochemically-active species is attached to the surface of a porous current collector (formed by electrodeposition) providing a strong connection from the active species to the substrate. Additionally, electrodeposition processes will be modified to enable the use of various electrochemically active species and substrates. This is a new initiative for FY2011.

STATUS OCT 1, 2010: In previous BATT efforts, significant progress was made in quantifying the energy and power advantages of three-dimensional electrode architectures over two-dimensional designs. Specifically, increased reversible capacity of Cu₆Sn₅ by electrodepositing Cu and Sn onto a Cu-foam electrode (also fabricated by electrodeposition) and manipulating the process to control the amount of free Sn in a composite Cu₆Sn₅-Sn electrode were reported.

STATUS SEP. 30, 2011: Three-dimensional architectures incorporating Sn and Cu, as well as other electrochemically-active elements and substrate materials, will have been designed. Processing parameters that control substrate porosity and conductivity will have been determined. Collaboration with industrially-interested partners will have been established.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

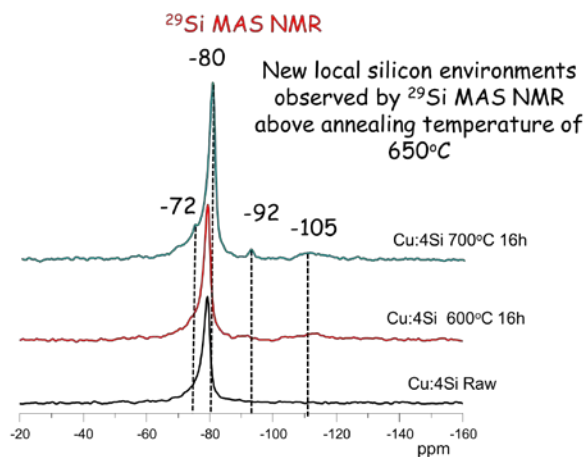
- (a) Prepare metal anode architectures by electrodeposition and determine their electrochemical properties in lithium half cells and full cells. (Sep. 11)**Complete**
- (b) Determine processing parameters that control substrate porosity and electrical conductivity within metal foams. (Sep. 11)**Complete**
- (c) Initiate studies into processes involved in electrodepositing materials into confined spaces. (Sep. 11)**On-going, due Sep. 12**
- (d) Establish contact with industry, and undertake comparative studies of commercial Cu foams. (Sep. 11)**On-going, due Apr. 12**

PROGRESS TOWARD MILESTONES

Our goal is to develop three-dimensional architectures for Li-ion battery anodes that can act to constrain the volume expansion that limits the cycle life of most main-group metal anodes.

Accomplishments: For FY2011, a series of metal-supported electrodes that use Si or Sn as the active element were developed and studied. Two separate techniques were developed that use Cu as both the conductive additive and the binder. In a series of studies based on Cu foams, synthetic parameters (including current density, time, additives, plating solution pH) were varied to determine how each variable translated to physical changes in the foam produced. During this study, metal foams were optimized with two different pore sizes. With these substrates, various amounts of Sn or Sb were deposited into the pores, annealed, and evaluated in an electrochemical cell. Post-test analyses determined the stability of the structures on cycling. In addition to three poster presentations, some of this work was recently published: *L. Trahey, et al., "Effect of Electrode Dimensionality and Morphology on the Performance of Cu₂Sb Thin Film Electrodes for Lithium-Ion Batteries," European Journal of Inorganic Chemistry, 3984 (2011)*. Initial results highlighted how the built-in porosity and confinement helped stabilize the electrode volume expansion while also increasing power capability when compared to planar electrodes of similar loading. In addition, work on developing a new electrode structure that could use micron-size Si as the active material was started. For these electrodes, Si was coated with Cu nanoparticles and, after binding the mixture to a Cu foil, it was annealed to create the desired phases. Initial work to characterizing the electrodes and under varying annealing conditions will continue. To date, it has been shown that by limiting the capacity to approximately 1000 mAh/g ("LiSi") the electrodes have a cycling stability and lifetime comparable to traditional PVdF electrodes but with a 75% drop in resistance. Work continues toward understanding how the phase formation in the interfacial region of the electrode affects cycling performance.

In this continuing effort, solid state ^{29}Si NMR has been used to characterize the phases formed at interfaces and in the bulk on the annealing of laminates and materials at various temperatures. Early work, in conjunction with XRD studies, has indicated that the predominant alloy phases formed as a result of long-term heating are Cu_3Si and Cu_4Si . MAS-NMR studies (F. Dogan, *et al.*, to be submitted) have indicated that the best cycling electrodes have very little alloy formation and little Si surface oxidation. Electrodes with larger numbers of Si species did not cycle as well as other electrodes. Since many silicon oxides are electrochemically inactive, their presence on the particle surface, introduced during the processing, may be blocking the Li insertion. In addition, some electrode samples showed peaks that can be associated with Cu_3Si . Work continues toward correlating the alloy presence to stability and cycling performance.



TASK 2.2 - PI, INSTITUTION: M. Stanley Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes – Anodes: Novel Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, safety, and volumetric capacity limitations of Li-ion batteries

OBJECTIVE: To replace the presently used carbon anodes with safer materials that will be compatible with low -cost layered oxide and phosphate cathodes and the associated electrolyte.

GENERAL APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites from bulk to nano-size. An understanding of the tin-cobalt anode, the only commercial anode besides carbon, will help us discover why amorphous nanomaterials work. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal, kinetic, and structural stability to gain an understanding of their behavior.

STATUS OCT 1, 2010: It has been shown that bulk crystalline metals have a high capacity and react readily with Li, but their capacity faded rapidly after several deep cycles in carbonate-based electrolytes; and their behavior was no better under shallow cycling. In contrast, it has been shown that amorphous nano-size Sn alloys, unlike pure Sn, have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like Co. It also has been shown that nano-size manganese oxides, unlike crystalline vanadium and manganese oxides, are possible anode candidates when SEI formers, such as LiBOB, are added to the electrolyte. It was shown that small amounts of Si enhance the cyclability of Al.

STATUS SEP. 30, 2011: The proposed work will result in the development of durable metal-based Li-ion battery anodes with volumetric energy densities that approach double those of the state-of-the-art carbons. Nano-tin materials will be synthesized by at least two different approaches and then characterized, determining their morphology and electrochemical behavior. Some clues will be found as to how to control the SEI on such materials to optimize lifetime.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit, and maximum system volume.

MILESTONES:

- (a) Synthesize nano-size tin materials by at least two different methods. (Mar. 11) **One method completed** and the other **delayed to Sep. 12**
- (b) Characterize these materials and determine their electrochemical behavior. (Sep. 11) **One method completed** and the other **delayed to Sep. 12**
- (c) Initiate studies on nano-silicon materials. Synthesize by at least one method. (Sep. 11) **Completed – studies on one material**

PROGRESS TOWARD MILESTONES

The goal of this project is to synthesize new Sn- and Si-based anodes that have double the volumetric capacity of the present carbons, without diminishing the gravimetric capacity. The expected status was achieved except as noted immediately below under milestones.

Milestones (a) and (b) nano-tin anodes. This quarter the synthesis and characterization of a Sn anode by one method was completed. The initial results were so promising that it was decided to move ahead on this compound and delay the second synthesis approach. The results are discussed below.

Milestone (c) nano-silicon anodes. The initial results on this anode, a Si/MgO/graphite (SMOG) composite synthesized by a two-step, high-energy ball-milling process were reported last quarter and published in ref (1) below.

Nano-sized, Sn-based alloy materials were prepared by mechanical milling using Ti, Al, and Mg as the reducing agents and different grinding media. It was found that both the reductive metal and grinding media significantly affect the material formed and the resulting electrochemical behavior. Titanium reduction provided materials with excellent capacity, 600 mAh/g, close to the theoretical capacity, and excellent capacity retention on cycling. The electrochemical behavior was further enhanced by the use of Fe-grinding media, which resulted in the alloying of some or all of the Sn with Fe giving Sn_2Fe . The capacity and rate capability of these Fe-containing materials is comparable to those of the Sn-Co-C compounds, and much better than bulk Sn_2Fe . The results are shown in Fig. 1 for materials synthesized by Ti reduction using soft-Fe-grinding media, where the Sn was present as nano-sized Sn_2Fe and the Fe came from the grinding media. The volumetric energy density is 2.2 Ah/cc, more than double that of carbon.

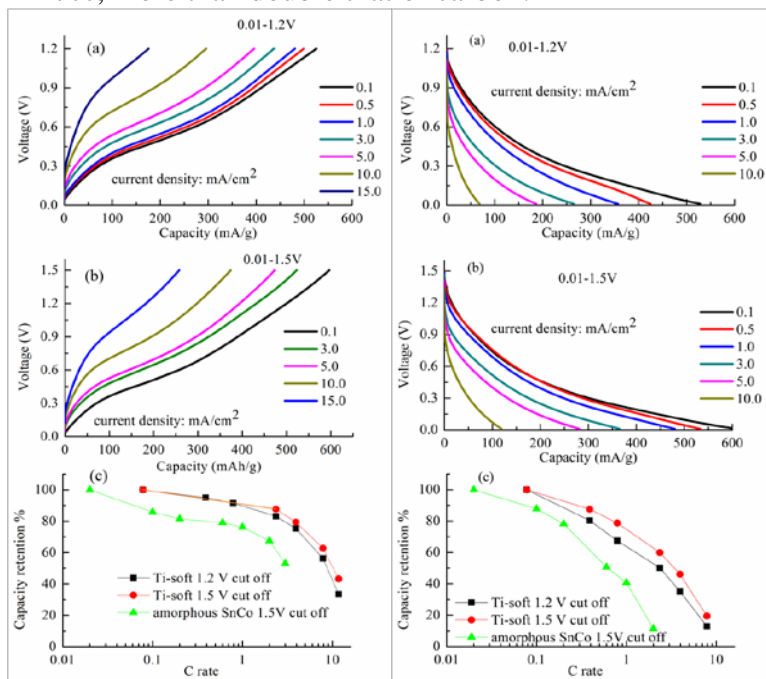


Figure 1.(left) Lithium removal and (right) lithium insertion into the Sn-Fe electrode synthesized by titanium reduction in soft-iron media. (a) cycled between 0.01 and 1.2 volts, (b) between 0.01 and 1.5 volts, and (c) Peukert plots comparing this material with the SONY SnCo anode (from ref (2)).

Publications in 2011:

1. Wenchao Zhou, Shailesh Upreti and M. Stanley Whittingham "High performance Si/MgO/graphite composite as the anode for lithium-ion batteries," *Electrochemistry Communications*, **13**, 158 (2011).
2. Ruigang Zhang, Shailesh Upreti and M. Stanley Whittingham, "Tin-Iron Based Nano-Materials as Anodes for Li-Ion Batteries," *J. Electrochem. Soc.*, in press.

TASK 2.3 - PI, INSTITUTION: Prashant N. Kumta, University of Pittsburgh

TASK TITLE - PROJECT: Anodes – Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low specific energy and energy density, poor cycle life and coulombic efficiency, large irreversible loss, poor rate capability, and calendar life.

OBJECTIVES: To identify new alternative nanostructured anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The objective is to replace carbon with an inexpensive nanostructured composite exhibiting higher capacity (1200 mAh/g) than carbon while exhibiting similar irreversible loss (<15%), coulombic efficiency (>99.9%), and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, cycle life, coulombic efficiency, and irreversible loss limitations of silicon-based electrodes.

GENERAL APPROACH: The approach is to search for inexpensive silicon, carbon, and other inactive matrix-based composite electrodes (powders rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of metallic Li, and 2) a capacity of at least 1200 mAh/g or greater (>2600 mAh/ml). Focus will be on exploring novel low-cost methods to generate nanoscale heterostructures of various silicon nanostructures and different carbon forms derived from graphitic carbon, nanotubes (CNT), and new binders. Other electrochemically inactive matrices will also be explored. Promising electrodes will be evaluated in half cells against metallic Li and compared to graphite as well as full cells. Electrode structure, microstructure, rate capability, long and short term cyclability, coulombic efficiency, as well as the origin and state of the SEI layers, will be explored.

STATUS OCT 1, 2010: Nano-scale electrodes comprising Si-graphitic carbon-polymer derived carbon and CNT-related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C structures exhibit stable capacities of 700-1000 mAh/g and higher.

STATUS SEP. 30, 2011: Efforts will continue to generate nano-composite ‘core-shell’, random, and aligned structures of varying nanoscale Si morphologies, boron (B), and C nanotubes exhibiting 1200 mAh/g and higher capacities. Research will be conducted to study the synthesis conditions, nano-scale microstructure affecting the energy density, rate capability, first cycle irreversible loss and coulombic efficiency, characterize the SEI layer, and outline steps to yield stable capacity, reduce irreversible loss, and increase coulombic efficiency.

RELEVANT USABC GOALS: Available energy for CD Mode, 10 kW Rate: 3.4 kWh (10 mile) and 11.6 kWh (40 mile); Available Energy for CS Mode: 0.5 kWh (10 mile) and 0.3 kWh (40 mile); 10s peak pulse discharge power: 45 kW (10 mile) and 38 kW (40 mile); Peak Regen Pulse Power (10 sec): 30 kW (10 mile) and 25 kW (40 mile); Cold cranking power at -30°C, 2sec-3 Pulses: 7kW; Calendar life: 15 years (at 40°C); CS HEV Cycle Life, 50 Wh Profile: 300,000 Cycles

MILESTONES:

- (a) Achieve stable reversible capacity of 1200 mAh/g or higher. (Mar. 11) **Complete**
- (b) Irreversible loss (<15%) and efficiency (>99.9%) to match carbon. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

In earlier reports, nanocrystalline or amorphous silicon (*nc/a*-Si) demonstrated enhanced capacity retention and cyclability, and the addition of novel composite coatings resulted in first cycle irreversible losses lower than the 15% goal. The response of *nc/a*-Si is due to free volume, the presence of defects, and the absence of long range order that result in a homogenous and less catastrophic volume expansion stress upon Li insertion. Hence, pulverization of Si is significantly reduced, resulting in good cyclability. In this regard, attempts were made to synthesize amorphous Si films directly on Cu foil by electro-reduction of a silicon halide-based electrolyte. A typical electrolyte comprised of 0.5 M SiCl_4 dissolved in PC and tetrabutylammonium chloride (TBACL), used as supporting electrolyte to improve the ionic conductivity. A three electrode set up was established, utilizing Cu rod of 11 mm dia. as the working electrode. A Pt foil and wire served as counter and reference electrodes, respectively. A linear sweep voltammogram (LSV) was obtained using the electrolyte and showed a cathodic peak at *ca.* -1.6 V vs. Pt. QRE (Fig.1), indicating the reduction of Si^{4+} to Si. This peak was not present in the LSV of the electrolyte in the absence of SiCl_4 . Additionally, small cathodic peaks at -1.8 and -0.92 V were observed in the electrolyte, attributed to the reduction of tetrabutylammonium ion (TBA^+) and trace amounts of HCl and H_2O , respectively.

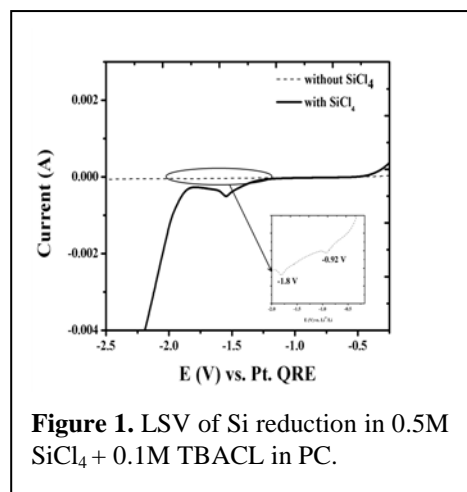


Figure 1. LSV of Si reduction in 0.5M SiCl_4 + 0.1M TBACL in PC.

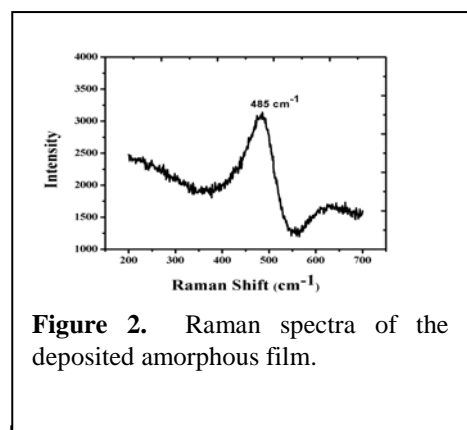


Figure 2. Raman spectra of the deposited amorphous film.

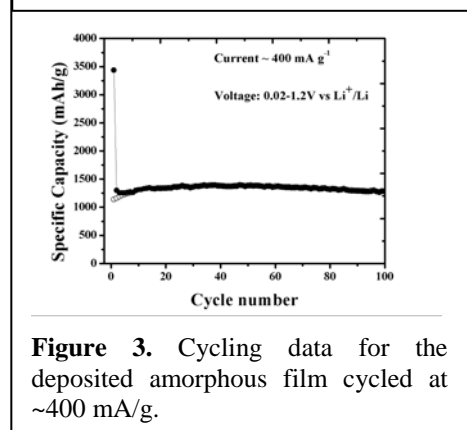


Figure 3. Cycling data for the deposited amorphous film cycled at ~ 400 mA/g.

to the desired 15% level observed in earlier reports on Si nanocomposites. After the 1st cycle, a stable reversible capacity of *ca.* 1300 mAh/g was obtained. The coulombic efficiency varied from 94 to 98% from the 2nd to 5th cycle, after which it improved and remained close to the desired goal of 99.9% for the remaining cycles. A capacity fade of *ca.* 0.016% per cycle was observed resulting in a capacity of *ca.* 1260 mA g^{-1} at the end of the 100th cycle. This approach of developing thin *a*-Si films directly on Cu eliminates the use of binders and conducting agents, rendering the process simple, facile, and amenable to large scale manufacturing.

TASK 2.4 - PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE – PROJECT: Anodes –Development of High Capacity Anode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, cost, poor cycle life and large irreversible capacity

OBJECTIVES: To develop high capacity, low cost anode with good rate capability to replace graphite in Li-ion batteries.

GENERAL APPROACH: Our approach is to manipulate the nano-structure and conductivity of Si and SiO_x to improve their mechanical and electrical stability. Both nano-sized and micro-sized Si particles with nano-pore structures will be investigated. The electronic conductivity of Si particles will be improved by CVD-coated carbon. Self-assembled templating method will be used to incorporate Si particles into graphene sheets to improve the electronic conductivity between Si particles and accommodate the volume variation of Si during cycling. The stability of SEI layers will be investigated by *in situ* TEM/SEM. New binders will be developed to improve the cyclability of a Si-based anode. Electrolyte and additives will be tailored to reduce the first cycle loss and stabilize SEI.

STATUS Oct. 1, 2010: Highly stable, free-standing SnO₂/graphene and TiO₂/graphene paper electrodes were successfully prepared with a unique self-assembly approach. These free-standing paper electrodes can operate with no extra current collector and conductive additive. Nano-TiO₂/Graphene composite demonstrated a capacity of ~170 mAh/g at 1C rate. SnO₂/graphene composite also demonstrated a capacity of ~790 mAh/g. Stable cycling and excellent rate capability were achieved in both composites. The electrochemical performance of nano Si and micro-sized Si particles with nano-pores was improved with a CVD-carbon coating. Self-assembled Si/graphene composites demonstrated a capacity of more than 1600 mAh/g Si for more than 35 cycles.

STATUS SEP. 30, 2011: The composition and cycling protocols of a Si/graphene hybrid electrode will be optimized to balance the high capacity and cycling stability. The initial irreversible capacity loss of a Si-based electrode will be minimized by adjusting the morphology/reactivity of the carbon matrix and developing new electrolyte/additives. Both conductive binders and pre-coated current collectors will be investigated to maintain a strong bonding among Si particles and between Si and current collectors during cycling.

RELEVANT USABC GOALS: >96 Wh/kg (PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:

- (a) Identify optimized carbon matrix/additives with reduced first cycle loss. (Mar. 11) **Complete**
- (b) Improve coulombic efficiency through appropriate electrolyte/additives. (Sep. 11) **Complete**
- (c) Optimize new conductive polymers as a binder for Si anode. (Sep. 11) **Delayed due to different Si sources and additives used, due Mar. 12.**

PROGRESS TOWARD MILESTONES

Most milestones for FY11 have been accomplished. A novel method was developed to synthesize Si nanoparticles from Si-containing precursors. A thin layer (*ca.* 5 nm) of CVD-coated-carbon stabilized the electric contact among silicon particles and increased the electrical conductivity of the Si anode. The porous Si with larger pore sizes demonstrated better cycle stability. Several different carbon additives and binders have been investigated. With 20% CMC binder and Ketjen black as the carbon additive, a specific capacity of 998 mAh/g (based on full electrode using porous Si) was obtained in 35 cycles. SiO_x anodes exhibited a stable capacity of *ca.* 600 mAh/g (based on full electrode) over 90 cycles.

A stable capacity of *ca.* 650 mAh/g (based on a full electrode) over 90 cycles was obtained by anchoring the Si onto a rigid, structural skeleton and then coating it with a conductive layer to provide continuous electrical contact (Fig. 1). A coin cell was tested between 0.02 and 1.5 V at a current density of *ca.* 1 A/g (the first three formation cycles were tested at a current density of 100 mA/g). The Si anode also had very good rate performance. Figure 2 shows the cycling performance under different current densities from 0.5 to 8 A/g. The capacity is *ca.* 500 mAh/g at the high rate of 8 A/g.

The effect of electrolyte additive, fluoroethylene carbonate (FEC), was studied using the nano-Si-based anode. With 10 wt% of FEC added in EC:DMC (1:2) electrolyte, the cycling stability of a Si anode was significantly improved. As shown in Fig. 3, there was almost no capacity fade over 70 cycles with the addition of FEC. In contrast, the cells with no FEC additive exhibited a capacity fade of *ca.* 50% after 70 cycles.

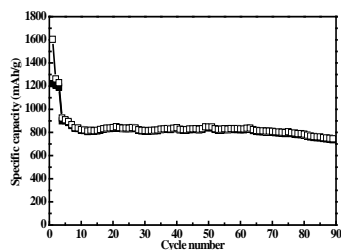


Figure 1. Stable cycling of Si anodes with rigid structural skeleton and continuous conductive carbon coating.

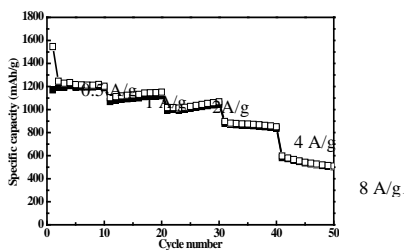


Figure 2. Si anode cycling at different current densities from 0.5 A/g to 8 A/g.

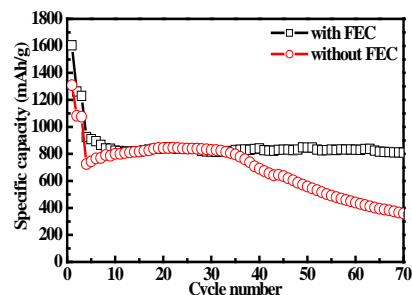


Figure 3. The effect of electrolyte additive fluoroethylene carbonate.

Further optimization of the uniformity of the Si loading on the rigid structure frame will be conducted. More work will be done to further improve the porous Si materials. The pore size effect and carbon additive effect will be investigated. Electrolyte additives will be further investigated to improve the cycle stability. The structure of the SEI layer with electrolyte additives will be systematically investigated.

Collaborations: I.A. Aksay, Princeton University, and Vorbeck Inc. have provided the graphene for this work. Prashant Kumta, University of Pittsburgh, assisted in depositing the Si nanoparticles on to novel carbon materials using CVD.

Publication:

Chong-Min Wang, Wu Xu, Jun Liu, Ji-Guang Zhang, Lax V. Saraf, Bruce W. Arey, Daiwon Choi, Zhen-Guo Yang, Jie Xiao, Suntharampillai Thevuthasan, and Donald R. Baer, "In Situ Transmission Electron Microscopy Observation of Microstructure and Phase Evolution in a SnO₂ Nanowire during Lithium Intercalation," *Nano Lett.*, **11** (5), 1874 (2011).

TASK 2.5 - PI, INSTITUTION: Anne Dillon, NREL; Steven George and Se-Hee Lee, University of Colorado, Boulder

TASK TITLE - PROJECT: Anodes – Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: Cost, low gravimetric and volumetric capacities, safety

OBJECTIVES: In this work we will utilize an inexpensive and scalable hot wire chemical vapor deposition (HWCVD) technique for the production of either amorphous silicon (a-Si) or nano-Si powders that are tailored for battery applications. We will also develop novel atomic layer deposition (ALD) coatings that will enable durable cycling to be achieved for the high volume expansion Si materials (~400 %)

GENERAL APPROACH: The a-Si or nano-Si powders will be fabricated with HWCVD *via* silane decomposition on a hot filament. Growth parameters will be explored to optimize yield and later incorporate dopants to produce more conductive a-Si as well as additives to improve cycling stability. Conventional electrodes containing active material, conductive additive and binder will be fabricated and subsequently coated via ALD that will serve as an artificial solid electrolyte interphase (SEI) and will importantly help minimize degradation upon volume expansion.

STATUS OCT. 1, 2010: This is a new award that will be initiated in FY11. However, following the BATT meeting at LBNL on July 27, 2010, Anne Dillon met with Yi Cui and Robert Huggins at Stanford to initiate a collaborative effort (July 28, 2010). It is believed that this will accelerate progress in both of these new Si awards. NREL and CU are already undergoing staffing plans to prepare for the new project. NREL is also currently slightly modifying the HWCVD apparatus that was previously used for photovoltaic applications.

STATUS SEP. 30, 2011: A thick Si anode with an ALD coating will be demonstrated to have a high durable capacity. Both gravimetric and volumetric capacities will be optimized.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES

- (a) Optimize HCVD produced a-Si or nano-Si in conventional coin cell. (Jan. 11) **Complete**
- (b) Demonstrate scale-up of HWCVD a-Si or nano-Si powder. (May 11) **Complete**
- (c) Demonstrate an ALD coating for improved performance of Si anode. (Jul. 11) **Complete**
- (d) Optimize coated electrode and demonstrate durable cycling. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

As reported previously, a novel technique that enables the creation of an electrode that is ≥ 30 to $40\ \mu\text{m}$ thick for a variety of different Si materials was developed. In this simple electrode configuration, Cu serves as both the binder and conductive additive. The technique has been employed to both amorphous Si and various different sizes of crystalline nanoparticles. In general, initial capacities of *ca.* 2500 mAh/g and a coulombic efficiency of *ca.* 95% are observed for all of the various materials.

As part of the coating focus group presentation in August, it was shown that by applying an Al_2O_3 coating to these materials, the initial capacity is reduced to *ca.* 1200 mAh/g but the coulombic efficiency is increased to $> 99\%$ (July milestone). Coating thicknesses from 0.5 to 2.5 nm were explored, and it was found that 1 nm is the optimal ALD Al_2O_3 coating thickness. Figure 1a shows that a 1 nm Al_2O_3 ALD-coated electrode containing commercial crystalline nano-Si particles has a capacity of over 1000 mAh/g for 150 cycles. Furthermore, there is *no* fade in the coulombic efficiency. The ALD coating may limit the Li insertion and simultaneously improve durability.

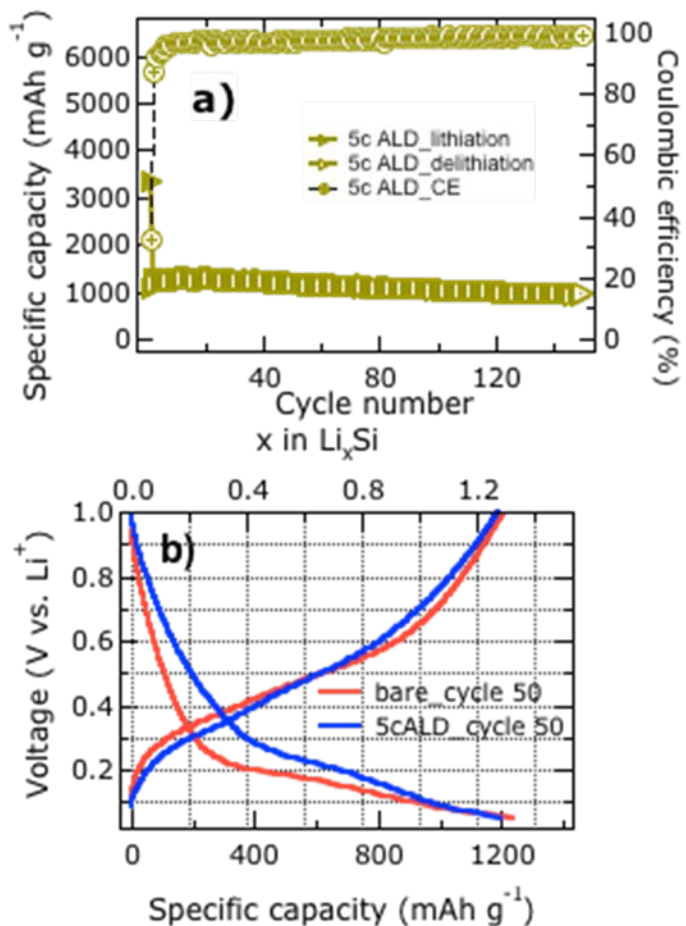


Figure 1. a) Durable cycling performance and Coulombic efficiency of an ALD coated nano-Si electrode employing our novel matrix with copper employed as both the conductive additive and binder. b) Voltage discharge and charge profiles of both bare and coated electrodes at cycle 50.

Figure 1b shows the voltage discharge and charge curves for a bare electrode and the coated electrode at the 50th cycle using the novel configuration. Note that the capacity of the bare electrode has faded to *ca.* 1200 mAh/g (from *ca.* 2500 mAh/g) and is now roughly the same as the coated electrode. Importantly, after only 2 cycles (not shown) the discharge curves look significantly more similar than those shown in Fig. 1b. Specifically, the Li⁺ insertion voltage drops over time for the bare electrode but not for the coated electrode. This indicates that the structure of the ALD-coated Si is not altered as much with cycling as that of the bare electrode. Thus, it is possible that limiting the number of Li⁺ ions that are inserted allows more structural integrity to be maintained and extends the durable cycling. Mechanistic studies to explain this phenomenon are currently underway.

TASK 2.6 - PI, INSTITUTION: Yury Gogotsi and Michel Barsoum, Drexel University

TASK TITLE - PROJECT: Anodes – New Layered Nanolaminates for Use in Lithium Battery Anodes

SYSTEMS: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC). To be compared with MAX phase and carbide-derived carbon anodes.

BARRIERS: Needs increased life, capacity and improved safety.

OBJECTIVES: Replace graphite with a new material. Layered ternary carbides and nitrides known as MAX phases - may offer combined advantages of graphite and Si anodes with a higher capacity than graphite, lesser expansion, longer cycle life and, potentially, a lower cost than Si nanoparticles.

GENERAL APPROACH: Since at this time the relationship between capacity and MAX phase chemistry is unknown; a rapid screening of as many MAX phases as possible will be carried out to find out the most promising chemistry, by testing their performance in lithium ion batteries. This will be guided by *ab initio* calculations. Reducing particle size, selective etching of A element out from the MAX structure, and exfoliation of these layered structure also will be investigated to increase the Li⁺ uptake of these structure and improve the Faradaic efficiency.

STATUS OCT 1, 2010: This project was initiated in January 2011.

STATUS SEP. 30, 2011: Select the most promising MAX phases from the 60-phase family (guided by *ab initio* calculations). Reduce the particle size to less than 1 micron and evaluate the effect of the particle size. Exfoliate MAX phases into nanolayers and conduct preliminary electrochemical studies using coin cells.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

(a) Complete theoretical investigation and conduct preliminary electrochemical screening of MAX phases. Demonstrate by modeling that MAX phases have a potential to surpass conventional carbon anodes (Jun. 11) **Abandoned due to change in research direction to concentrate on MXenes (exfoliated MAX phases) instead of pristine MAX phases.**

(b) Produce porous anodes of MAX phase that require neither binder nor carbon black additives (Jun. 11) **Complete**

(c) Achieve particle size reduction and exfoliation of MAX phases into graphene-like 2-D structure “MAXene” (Sep. 11) **Complete**

(d) Conduct a complete electrochemical characterization of MAX phases and demonstrate the effect of vacancies in the metal sublattice on lithium uptake by the anode. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Given the change of direction - from MAX to MXene - it is difficult to directly assess how close we are to our Expected Status section described on page 1. This change of direction was dictated by the fact that the Li uptake of the MXenes was about a factor of 5 higher than that of the MAX phases (see below). Given that the overarching goal is to produce materials that perform better than graphite, then the results shown below clearly indicate that we have achieved, if not exceeded, our Expected Status described on page 1. At this stage we are within a factor of 2 or 3 of the capacity of graphite.

Following the successful exfoliation of Ti_3AlC_2 to 2-D Ti_3C_2 structures, that was reported in the Q3 report, a more in-depth study of the kinetics of exfoliation was carried out on Ti_3AlC_2 . It was found that complete exfoliation of Ti_3AlC_2 (particle size $> 53\ \mu\text{m}$ and $< 65\ \mu\text{m}$) with HF treatment for 2 h occurs at temperatures above 50°C . At room temperature the process takes about 15 h. For particles $< 40\ \mu\text{m}$ complete exfoliation was possible in about 2 h in a 50% aqueous HF solution at room temperature.

Significant progress is being made in exfoliating other MAX phases into MXenes with different chemistries. Both sets of results are being prepared for publication.

Electrochemical measurements for Li^+ uptake for six different MAX phases (Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC , Ti_2SC , Ti_2SnC , Zr_2InC) showed low capacity (around 30 mAh/g). By contrast, exfoliated Ti_3AlC_2 powders showed a capacity of 250 mAh/g for the first cycle and a reversible capacity 5 times higher than pristine Ti_3AlC_2 (Fig. 1). These results justify the change in research direction to focus on exfoliated MAX phases or MXenes, with significantly better Li^+ uptake.

The irreversibility of the first cycle can be explained by the presence of hydroxyl (OH) groups on the MXene surface sheets, which presumably react with Li. At this point, work is progressing on reducing those OH groups to enhance the overall Li capacity. Note that the capacity in Fig. 1 was divided by the total overall weight of the electrode including the MXene, carbon black, and binder.

At this time, it is reasonable to assume that exfoliated Ti_2AlC would have a Li capacity that is 1.5 times higher than Ti_3AlC_2 , due to the lower number of atomic layers per each MXene sheet (3 atomic layers in case of Ti_2C vs. 5 for Ti_3C_2). As noted above, significant progress has been achieved in exfoliating Ti_2AlC and other MAX phases. Another high impact paper is anticipated.

During this past quarter, we had 5 refereed papers published or in print. The most important paper is a feature article in – and on the cover of *Advanced Materials*. This paper has garnered some positive press (<http://max.materials.drexel.edu/mxene—a-new-family-of-2-d-transition-metal-carbides-and-nitrides/>).

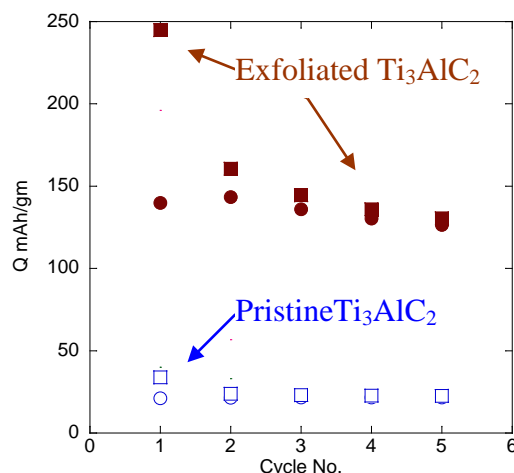


Figure 1. Lithiation and de-lithiation capacity vs. cycle number for pristine Ti_3AlC_2 and exfoliated Ti_3AlC_2 .

Task 2.7-PI, INSTITUTION: Donghai Wang and Michael Hickner, Penn State University

TASK TITLE: Anodes: Synthesis and Characterization of Polymer-Coated Layered SiO_x -Graphene Nanocomposite Anodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF_6 +EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor capacity cycling, large initial irreversible capacity and corresponding low coulombic efficiency.

OBJECTIVES: To mitigate the electrochemical limitations of SiO_x anodes during charge/discharge by designing novel SiO_x -graphene nanocomposite coated with polymer to tolerate volume change, improve electrode kinetics, and decrease initial irreversible capacity loss. The new materials proposed and optimized fabrication strategies will improve the performance of SiO_x -based anodes.

GENERAL APPROACH: Our approach is to synthesize layered SiO_x -graphene nanocomposites composed of alternating layers of graphene sheets and SiO_x nanoparticles to tolerate volume change upon lithiation/delithiation while maintaining Li-ion conductivity. Novel polymer binders will be developed with controlled elastic properties, ion-conductive moieties, and SiO_x surface binding functionality, in order to stabilize and bridge SiO_x particles. To improve the initial coulombic efficiency, two approaches will be adopted. First, block copolymer binders with lithiated polyethylene oxide blocks will be used to compensate for Li consumption upon irreversible conversion of SiO_x into Li_2O and Li silicates. Second, chemical lithiation methods will be used to prelithiate SiO_x -graphene nanocomposites into $\text{Li}_y\text{Si}_x\text{O}$ -graphene.

STATUS OCT. 1, 2010: This project was initiated on January 1, 2011.

STATUS SEP. 2011: SiO_x nanoparticles with controlled particle sizes will be synthesized. Novel polymer binders with controlled SiO_x binding groups and Li-conducting blocks will be synthesized. SiO_x -graphene nanocomposite anodes will be demonstrated. Processing parameters that control nanoparticle size and polymer functionality will have been determined.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

- (a) Prepare SiO_x nanoparticles with controlled particle size, *e.g.*, ranging from 5 to 20 nm and demonstrate SiO_x -graphene hybrids with novel polymer binders. (Jun. 11)**Complete**
- (b) Determine electrochemical properties of SiO_x nanoparticle, SiO_x -graphene hybrids and the polymer binders in lithium half cell. (Sep. 11)**Complete**
- (c) Obtain 40% first cycle capacity as well as 90% coulombic efficiency cycle to cycle thereafter. (Sep. 11)**Complete**

PROGRESS TOWARD MILESTONES

Si-based anode materials: Efforts toward the synthesis of Si/graphene hybrids were continued this quarter. Silicone nanoparticles with an average particle diameter of 50 to 100 nm were synthesized. To obtain Si/graphene hybrids, the resulting Si nanoparticles were mixed thoroughly with functionalized graphene sheets followed by a thermal treatment. The TEM image of Si/graphene hybrids (Fig. 1a) revealed that Si nanoparticles were well distributed onto the graphene conductive support.

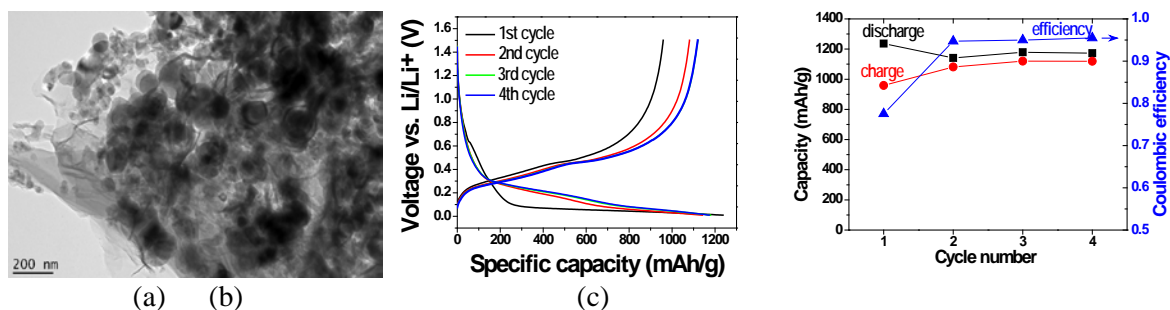


Figure 1. (a) TEM image, (b) anode performance of as-prepared Si/graphene hybrids, and (c) capacity and coulombic efficiency *versus* cycle number for the Si/graphene hybrids.

Electrochemical tests were performed on as-prepared Si/graphene hybrid anode materials (Fig. 1b). It was found that Si/graphene hybrids exhibited a discharge capacity of above 1200 mAh/g for the first cycle at 0.3 mA/cm² (equivalent to a C/10 rate); a stable capacity of *ca.* 1150 mAh/g was obtained in the following cycles. Compared with the fast capacity fade of the commercial Si and as-prepared Si nanoparticles, the cycle stability of Si/graphene hybrids was an improvement (Fig. 1c). Further investigation on the anode performance of Si/graphene hybrids is underway.

Polymer binders:

Radel-based binders have been screened for their initial performance and their capacity retention under long-term cycling (Fig. 2). PVDF and CMC/SBR had the highest initial capacities of the binders surveyed thus far, but the 10th cycle performance of PVDF was very poor. CMC/SBR showed better 10th cycle capacity than PVDF, and the Radel binders showed good performance for both unfunctionalized and sulfonated samples. The sulfonated Radel sample showed a lower initial capacity, perhaps due to the presence of the ionic groups. However, the 10th cycle capacity of the sulfonated polymer was the best of all samples tested, perhaps due to interactions with the Si nanoparticle anodes. Interestingly, Radel, with no specific interactions with Si, showed performance similar to that of CMC/SBR. Future work will entail longer cycling protocols of up to 200 cycles.

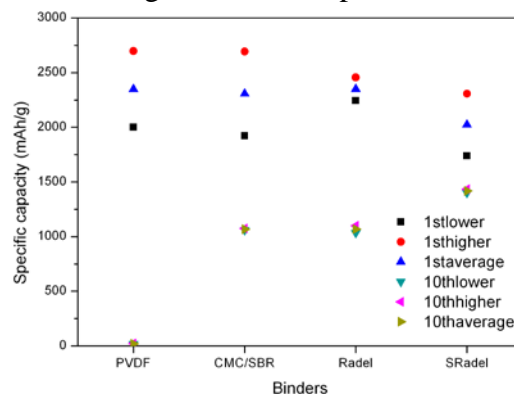


Figure 2. 1st cycle and 10th cycle capacities of Si anodes with different binders.

TASK 2.8 - PI, INSTITUTION: Yi Cui, Stanford University

TASK TITLE - PROJECT: Anodes – Wiring up Silicon Nanoparticles for High Performance Lithium Ion Battery Anodes

SYSTEMS: Conoco Phillips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor low-temperature operation, and abuse tolerance limitations

OBJECTIVES: To overcome the charge capacity limitation of conventional carbon anodes by designing a nano-architected silicon electrode. This anode can address the issues caused by the volumetric expansion of the materials and provide a good cycle life.

GENERAL APPROACH: This project explores a hierarchical porous electrode concept to wire up Si nanoparticles as novel lithium ion battery anodes. Specifically, this project engineers well-controlled holes with a variety of sizes into Si particle electrodes to allow for facile strain relaxation. This project also develops a simple method to connect all the nanoparticles electrically to the metal current collector, which remain connected after long-term cycling. This project further explores strategies to produce stable SEI layer for long term cycling. This project was initiated January 1, 2011.

STATUS OCT 1, 2010: This project was initiated January 1, 2011.

STATUS SEP. 30, 2011: Critical diameters vs. charge capacity without breaking will have been identified. Detail understanding on volume expansion will have been established. Methods of forming porous Si anodes will have been designed. The method of connecting Si nanoparticles will have been developed.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

- (a) Identify the method to connect Si nanoparticles electrically (Jun. 11). **Complete**
- (b) Find out the relationship of critical breaking size versus capacity for deep lithiation (Sep. 11) **Complete**
- (c) Identify a method to produce porous Si electrodes (Sep. 11) **Complete**
- (d) Obtain detailed information on the volume expansion and contraction of Si. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Determining size effects on fracture upon electrochemical lithiation/delithiation of silicon nanopillars. The circumstances causing the fracture of Si nanostructures during lithiation/delithiation are not completely understood. To determine the effect of nanostructure size and structure on fracture characteristics, nanopillars with controlled size and crystallographic orientation were fabricated and observed with SEM after lithiation/delithiation. Surprisingly, it was found that many nanopillars fractured upon initial lithiation, which has not been predicted by many computational simulations. Pillars with $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ axial orientations all show cracks that run along their length after lithiation. Interestingly, the cracks are usually located between directions of preferred radial anisotropic expansion. Because of this, it is proposed that the cracks develop due to regions of concentrated tensile hoop stress between the preferred radial expansion directions. In addition, it was found that pillars with diameters > 360 nm consistently fractured upon lithiation, while pillars with diameters < 240 nm usually did not fracture. The fraction of fractured pillars was dependent on lithiation rate only for pillars of intermediate diameter (240 nm). Overall, these data indicate a critical size for fracture upon lithiation between *ca.* 240 and 360 nm.

Conductive, mechanically robust, electrochemically inactive nanoscale scaffolding for supporting Si active material. Titanium carbide/carbon core-shell nanofibers were fabricated directly on a steel substrate, and then CVD was used to coat amorphous Si onto this scaffolding (Fig. 1). The nanoscale electronically conductive scaffolding allows for relatively high mass loading and good electronic connectivity, and the large mechanical stiffness and strength of the TiC/C nanofibers permit the Si to mechanically deform during alloying/dealloying without damaging the underlying conductive backbone. This is in contrast to other one-dimensional nanostructures, such as Si nanowires, in which the entire structure reacts with Li during charge/discharge and is altered in the process. The specific capacity data with cycling shown in Fig. 1 shows that a capacity close to 2800 mAh/g can be maintained after 100 cycles for the TiC/C/Si composite (red dots), which exceeds that of Si nanowires (black dots). The coulombic efficiency is also improved compared to Si nanowires. This study shows the importance of interfacing large volume-expansion alloying anode materials with mechanically robust inactive materials for good battery performance.

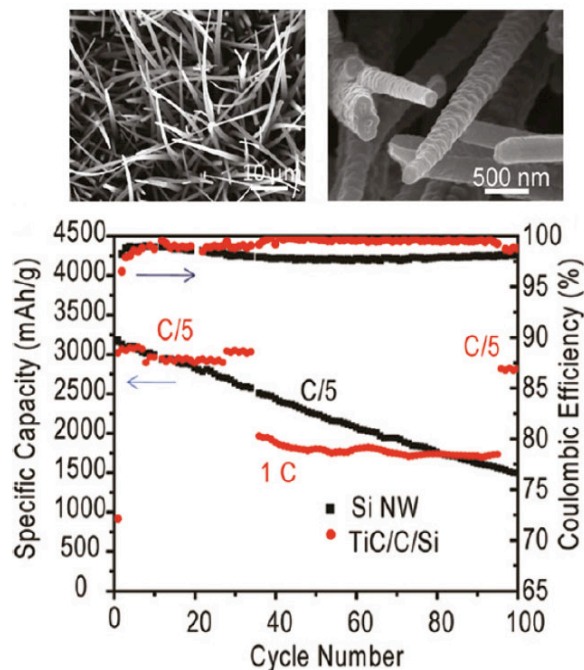


Figure 1. SEM images of TiC/C nanofibers after Si deposition and specific capacity with cycling.

TASK 2.8 - PI, INSTITUTION: Kwai Chan and Michael Miller, Southwest Research Institute

TASK TITLE - PROJECT: Anodes – Synthesis and Characterization of Silicon Clathrates for Anode Applications in Lithium-Ion Batteries

SYSTEMS: Conoco Phillips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, low-power density, and short calendar and cycle lives

OBJECTIVES: The objectives are to synthesize and characterize silicon clathrate anodes designed to exhibit small volume expansion during lithiation, high specific energy density, while avoiding capacity fading and improving battery life and abuse tolerance.

GENERAL APPROACH: Our approach is to synthesize guest-free Type I silicon clathrate (Si₄₆, space group $Pm\bar{3}n$) using high-pressure, high-temperature experimental methods, while concurrently exploring an investigational route for direct synthesis of guest-free clathrate and performing *ab initio* and classical molecular dynamics (MD) computations to identify lithiation pathways. The silicon clathrates will be utilized to fabricate prototype silicon clathrate anodes. Electrochemical characterization will be performed to evaluate and improve, if necessary, anode performance including cyclic stability. The final year of the program will be directed at the design, assembly, and characterization of a complete (anode/cathode) small-scale, prototype battery suitable for concept demonstration.

STATUS OCT 1, 2010: This project will be initiated January 1, 2011.

STATUS SEP. 30, 2011: small quantities (1-2 grams) of Type I clathrates will have been synthesized via one of two synthesis methods: (1) high-temperature, high-pressure method, and (2) direct solution method. Computational results will have been obtained using first principles (CPMD) and classical theories to identify possible reaction pathways for the formation of clathrates, Li_xSi₄₆, and Li₁₅Si₄ by investigating (1) the thermodynamic and kinetic constraints associated with structural transformation of BaSi₂ to Ba₈Si₄₆, and (2) the energy and dynamics associated with exchanging Ba²⁺ with Li⁺.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

- (a) Prepare 1-2 gram quantities of Type I clathrates by one or both synthesis methods (Jun. 11). **Complete**
- (b) Select one synthetic pathway (Sep. 11). **Delayed, due Dec. 11**
- (c) Identify possible reaction pathways (based on modeling results) for the formation of empty clathrates Si₄₆, Li_xSi₄₆, and Li₁₅Si₄ (Sep. 11). **Complete**
- (d) Construct and evaluate an electrochemical half-cell device using silicon clathrate materials synthesized in Year 1 (Sep. 11). **Complete**

PROGRESS TOWARD MILESTONES

Task 1 – Synthesis of Guest-Free Silicon Clathrate I

Batch Synthesis via Soft Oxidation of BaSi_2 : A synthetic pathway was designed and the necessary hardware (manifolds and glass reactor) was set up to proceed with direct batch-synthesis of guest-free silicon Type I clathrates at elevated temperature. First, the thermochemical stability of candidate ionic liquid (IL) solvents needed to carry out the synthesis at temperatures at or slightly above 300°C for periods in excess of 48 hours was evaluated. Differential scanning calorimetry coupled with thermal gravimetric analysis (DSC-TGA) showed that the PF_6^- salt of 1-butyl-3-methylimidazolium will not be sufficiently stable for the reaction due to its degradation onset near 300°C . Subsequently, an alternate proprietary IL, consisting of the bis-(trifluoromethylsulfonyl)imide anion was discovered to show excellent thermochemical stability up to 400°C over 48 hours with negligible mass loss. This IL was incorporated into the reactor setup. Synthesis of guest-free silicon clathrates *via* soft oxidation of BaSi_2 was initiated.

High-pressure, High-temperature Multianvil Synthesis: Based on encouraging results reported in the 2nd Quarter, high-pressure, high-temperature multi-anvil synthesis of $\text{Ba}_8\text{Si}_{46}$ was continued to produce sufficient quantities (2 gm) of materials for electrochemical evaluation.

Sufficient amounts (about 12 gm) of clathrates were produced by arc-melting to allow half-cells to be made and Task 4 to proceed on schedule. Decision on the feasibility of other reaction pathways (bath synthesis, high-pressure, high-temperature multi-anvil synthesis, and direct synthesis by PEMS) is delayed until December 30, 2011 since multiple tests are still on-going.

Task 2 – Molecular Modeling of Silicon Clathrates

The possible routes for extracting Ba atoms from $\text{Ba}_8\text{Si}_{46}$ and $\text{Ba}_8\text{Al}_6\text{Si}_{40}$ were investigated by performing first-principal energetic computations using the Car-Parrinello molecular dynamics code. The energy change due to the presence of a guest Ba atom residing in a Si_{46} cage or an alloyed $\text{Al}_6\text{Si}_{40}$ cage was computed as a function of the number of Ba atoms. The results, shown in Fig.1, indicate that the energy required to extract a Ba atom from the Si_{46} or $\text{Al}_6\text{Si}_{40}$ cage ranges from 2.43 eV to 3.66 eV at 0 K. The energy change was also computed as a function of temperature to identify potential pathways and processing windows for extracting guest Ba atoms from the clathrates.

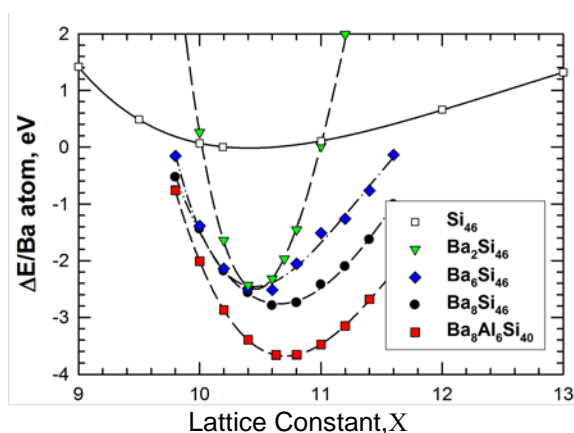


Figure 1. Energy change of Si_{46} due to Ba guest atoms or Al alloying.

Task 4 – Half-Cell Electrochemical Characterization

A method was devised this quarter to fabricate anodes consisting of previously synthesized $\text{Ba}_8\text{M}_6\text{Si}_{40}$ conformed to *ca.* 1 cm thin disks. Specifically, the anode material was pulverized to very small particle size using a simple mini-ball and capsule anvil system. The fine powders were then pressed into a thin disk in a mini-press apparatus. Mechanically stable anode-disks were successfully prepared without the use of any binder material. A method was also devised to bond the pressed disk to a current collector (metal foil) for use in an electrochemical half-cell apparatus. A three-electrode bulk-electrolysis cell arrangement was used to deintercalate Ba^{2+} from the electrode material. Subsequently, Li was intercalated into the clathrate anode to evaluate the capacity. The tests are still on-going. Preliminary results indicated that Ba^{2+} ions were extracted during oxidation and Li^+ ions were inserted into the anode during reduction.

BATT TASK 3

ELECTROLYTES

TASK 3.1 - PI, INSTITUTION: Nitash Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes – Development of Polymer Electrolytes for Advanced Lithium Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Improved energy density and safety.

OBJECTIVES: Characterize PS-PEO electrolytes with LiTFSI against Li-metal anodes in symmetric cells, sulfur, and air cathodes. Use block copolymers to create mesoporous battery separators for conventional liquid electrolytes.

GENERAL APPROACH: Synthesize and characterize dry PS-PEO (and PS-PEO-PS) polymer electrolytes. Continue to characterize salt/polymer mixtures by AC impedance spectroscopy, and make DC measurements with Li | polymer electrolyte | Li cells to obtain diffusion coefficients and Li transference numbers. Collaborate with members of the BATT Program to test stability of the electrolyte against electrodes (Li metal, sulfur, and air). Synthesize and characterize porous PS-PE polymer separators by synthesizing a block copolymer, blending with a homopolymer, and washing out the homopolymer to yield a porous block copolymer.

STATUS OCT. 1, 2010: Completed study of effect of morphology on diffusion coefficient and solubility of Li₂S_x in PS-PEO copolymers. Used membrane casting device to create first Li|polymer, electrolyte|air cells. Identified ideal molecular weight of homopolymer for creating block copolymer-based separators. Initiated project on electronically- and ionically-conducting polymer binders.

STATUS SEP. 30, 2011: Complete study of effect of morphology on transference number and diffusion coefficients in PS-PEO copolymers. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores. Study polysulfide dissolution in Li|SEO|S cells. Study the effect of cathode composition and morphology on Li|SEO|air cells. Synthesize copolymers that conduct both electrons and ions.

RELEVANT USABC GOALS: EV applications goals are a specific energy of 200 Wh/kg and a specific pulse power of 400 W/kg.

MILESTONES:

- (a) Measure transference number as a function of morphology of SEO. (Mar. 11) **Complete**
- (b) Complete synthesis of electronically- and ionically-conducting binder (Jun. 11) **Complete**
- (c) Report on cycling characteristics of Li|PS-PEO|air cells as a function of cathode composition and morphology. Go/no go decision based on improvement of one of the key limitations of current Li/air cells: capacity fade due to water contamination. (Sep. 11) **Complete**
- (d) Quantify the relationship between conductivity and morphology of porous block copolymer separators (Sep. 11). **Complete**
- (e) Quantify the effect of nanostructure on thermodynamics of SEO/polysulfide thermodynamics (Sep. 11). **Complete**

PROGRESS TOWARD MILESTONES

Measurements for milestone (a) are finished and the milestone is considered complete. The measurements were performed on SEOs with a variety of morphologies and different domain spacings, using both a rigorous electrochemical method and pulsed-field-gradient NMR. These measurements suggest that the Li^+ transference number for SEO block copolymers is 0.6 ± 0.1 , which is similar to the value measured for PEO homopolymer. Figure 1 shows the open-circuit potential of concentration cells in which one half consisted of SEO5 with a fixed concentration ($r = [\text{Li}]/[\text{EO}] = 0.085$) against SEO5 samples with $0.05 \leq r \leq 0.115$, showing a monotonically-decreasing potential with increasing r , as expected.

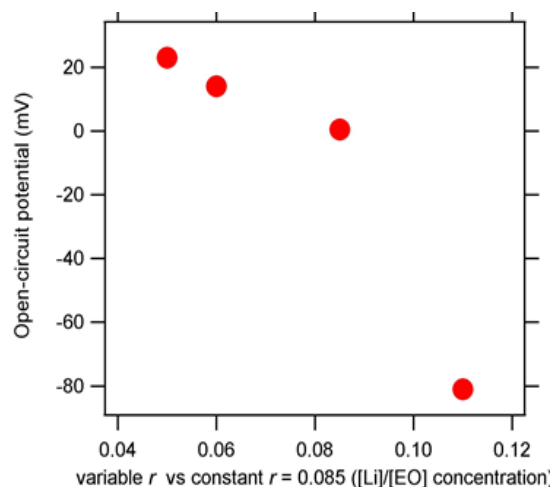


Figure 1. Sample concentration cell data for electrochemical measurements (milestone a).

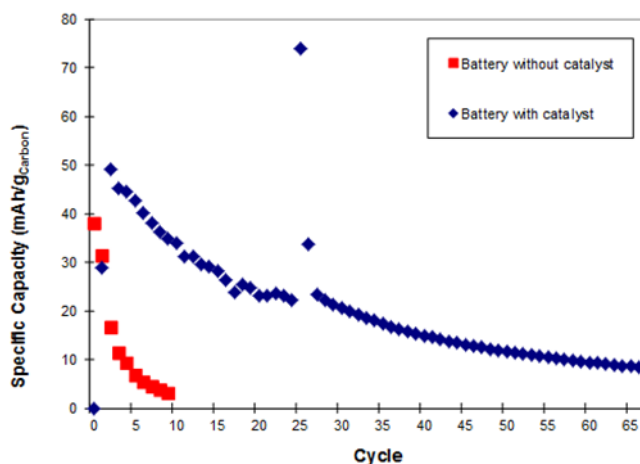


Figure 2. Comparison of Li-SEO-Air batteries with and without catalyst in air cathode (milestone b).

Milestone (b) has been completed, the results of which was summarized in the following publication: A.E. Javier, S.N. Patel, D.T. Hallinan, V. Srinivasan, and N.P. Balsara, “Simultaneous Electronic and Ionic Conduction in a Block Copolymer: Application in Lithium Battery Electrodes,” *Angew. Chem. Int. Ed.*, **50**: 9848–9851 (2011).

Milestone (c) has been completed. Cycling tests show promising improvement based on recently synthesized catalyst materials. Water contamination has become a non-issue due to a change in battery configuration. Combining MnO_2 and Au catalyst nanoparticles led to narrowed cycling voltage limits while maintaining similar capacity. Figure 2 also shows significant reduction in capacity fade as compared to batteries with no catalyst.

Milestone (d) has been completed and a manuscript discussing the impact of changing α ($\alpha = N_{\text{PS,Homo}}/N_{\text{PS,BCP}}$) on conductivity is under review by the *Journal of Membrane Science*. Current experiments aim to study the effect of changing the size of the block copolymer components on conductivity. Three block copolymers with identical $N_{\text{PS,BCP}}$, but different $N_{\text{PE,BCP}}$ have been synthesized and their conductivities in liquid electrolyte are being measured at different α values. Other experiments include RSoXS, which is used to distinguish between PS/PE morphology and polymer/hole morphology.

Milestone (e) is complete. Initial Li|SEO|S cell testing has begun. Previous work has been reported in the following manuscripts: “Effect of Molecular Weight on Conductivity of Polymer Electrolytes,” by A.A. Teran, *et al.*, which was accepted to *Solid State Ionics* (doi:10.1016/j.ssi.2011.09.021) and “Effect of Lithium Polysulfides on the Morphology of Block Copolymer Electrolyte,” by A.A. Teran and N.P. Balsara, currently under review for publication in *Macromolecules*.

TASK 3.2 - PI, INSTITUTION: John Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes – R&D for Advanced Lithium Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor cycle and calendar life, low power and energy densities, particularly at low temperatures (-30°C)

OBJECTIVES: 1) Determine the role of electrolyte structure upon bulk transport and intrinsic electro-chemical kinetics and how it contributes to cell impedance (Energy/ power density). 2) Determine chemical and electrochemical stability of electrolyte materials to allow elucidation of passivating layers (*e.g.*, SEI).

GENERAL APPROACH: A physical organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the processes that may affect the performance of the battery. This involves model compounds as well as synthesis of new materials to test hypotheses which may explain battery behavior.

STATUS OCT 1, 2010: Reactivity of salt anions is a major contributor to interfacial impedance and the structure can be altered to reduce this. The behavior of single-ion conductor polyelectrolytes with cathodes was explored to confirm the benefits of such electrolyte systems with regard to electrode thicknesses and increased energy density. Silicon and tin alloy anodes were studied to evaluate the benefits of polyelectrolytes on large volume-change electrodes.

STATUS SEP. 30, 2011: Studies on composite electrodes using single-ion conductor binders will continue with the focus area materials: high voltage Ni-Mn spinel cathodes and Conoco Philips CPG-8 graphite anodes. The behavior of the single-ion binders will be compared with the base-line electrolytes. Detailed chemical analysis of the electrolyte degradation products will be completed. Work on high volume expanding anodes with single-ion conducting binders will be extended using Si-based alloys. Dry polymer systems will be tested with LiFePO₄.

RELEVANT USABC GOALS: *Available energy:* 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power:* 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life:* 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life:* 15 years (at 40°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:

(a) Determine whether available single-ion conductor polyelectrolytes function with the high voltage NiMn spinel cathodes. (Apr. 11) **Complete**

(b) Determine the stability of base-line and single-ion electrolyte to NiMn spinel cathodes, including chemical analysis of electrolyte degradation products. (Sep. 11) **Partially complete; due Dec. 2011**

PROGRESS TOWARD MILESTONES

The single-ion conductor (SIC) material with the structure shown in Fig. 1a) was used in gel form with EC/EMC solvents. The material was prepared as a composite electrode with LiFePO_4 and its electrochemical stability is shown in Fig. 1b). This experiment shows that the materials are capable of stable performance with high voltage electrodes and constitutes a partial accomplishment of Milestone b). Full accomplishment is in process with NiMn Spinel electrodes and will be completed next quarter.

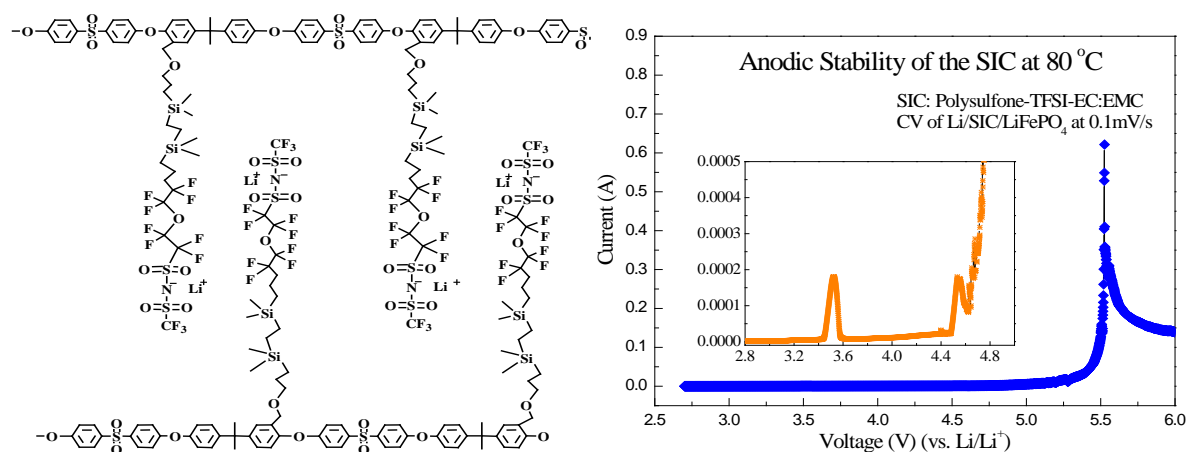


Figure 1. Structure of imide anion single ion conductor based on polysulfone backbones; b) electrochemical stability of SIC material 1a) in LiFePO_4 composite electrodes.

The behavior of the SIC electrolyte was tested using various electrode thicknesses and the material exhibited the expected benefits of thicker composite electrode access. Experiments were carried out to compare the behavior of the SIC with binary salt electrolytes. The impedance is shown in Fig. 2a) and the discharge behavior at different rates is shown in Fig. 2b) where it can be clearly seen that the SIC material reduces the polarization within the electrode particularly at high rates thus allowing more of the electrode to be accessed as predicted by Newman. These experiments represent accomplishment of delayed milestone a) from FY2010.

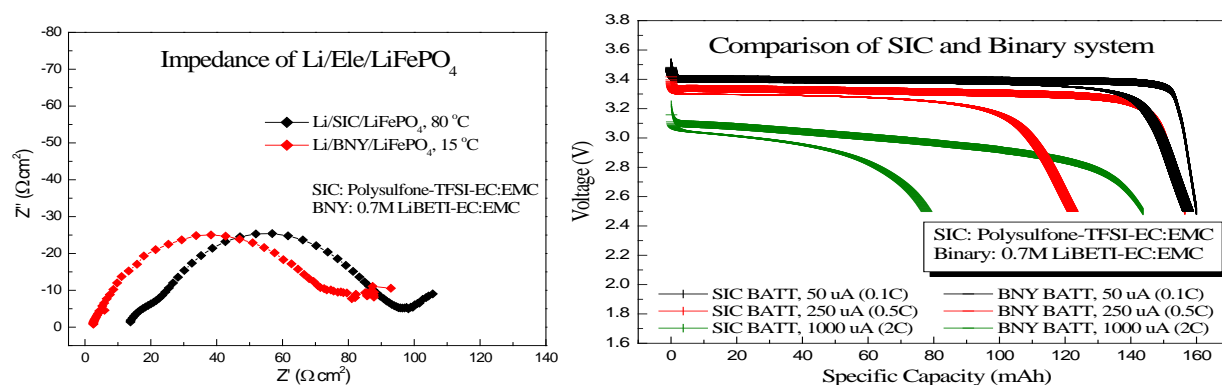


Figure 2. a) Comparison of impedance of the SIC cell described in Figure 1 with a binary salt electrolyte cell; b) comparison of discharge behavior for SIC cell with binary salt cell.

TASK 3.3 - PI, INSTITUTION: Dmitry Bedrov and Feng Liu, University of Utah

TASK TITLE - PROJECT: Electrolytes – Modeling: Molecular Modeling of Electrodes, SEI, Electrolytes, and Electrolyte/Electrode Interfaces

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor low temperature operation, transport through SEI layer and cycle life. High interfacial resistance. Low energy and power density.

OBJECTIVES: Prediction and investigation of structure and formation of the SEI at high energy density anodes using reactive MD simulations. Prediction and understanding of properties of novel high voltage electrolytes including oxidative stability and degradation products on the cathode. Prediction and understanding of charge transfer resistance to graphite and LiFePO₄ electrodes. Improved understanding of electric double layer structure, capacitance and transport as a function of electrode potential and temperature.

GENERAL APPROACH: Utilize developed force fields and simulation methods to simulate high voltage novel electrolytes. Utilize electroactive interface model to study electric double layer properties and charge transfer processes at the cathode/electrolyte and anode/electrolyte interfaces. Utilize reactive force field (ReaxFF) methods to study SEI formation at model anodes with emphasis on additives and electrolyte oxidation at model cathodes.

STATUS OCT 1, 2010: All codes and models except for parameterization of ReaxFF for electrolyte oxidation at cathode surfaces are in place. Initial novel electrolytes and additives of interest were determined, based upon consultation with other BATT investigators. All systems to be studied in investigations of SEI structure, anode charge transfer resistance, cathode charge transfer resistance, electric double layer structure, capacitance and transport were determined and implemented.

STATUS SEP. 30, 2011: All simulations associated with prediction of SEI structure on model anodes, prediction of charge transfer resistance at model cathode and anode interfaces, including whole cell simulations will be completed. Simulation studies of novel electrolytes in collaboration with BATT investigators will be complete. Studies of electrolyte oxidative stability at model cathode interfaces will be finalized.

RELEVANT USABC GOALS: *10-s discharge power:* 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:

- (a) Complete investigation of electric double layer structure and charge transfer resistance as a function of electrode potential for model electrodes. (Feb. 11) **Complete**
- (b) Complete investigation of conductivity of novel high voltage electrolytes. (Apr. 11) **Complete**
- (c) Complete study of SEI formation and role of additives for model anodes. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Our reactive MD simulations have demonstrated that various alkyl carbonates are formed in the outer SEI layer at the anode due to single electron reduction. To improve our understanding of Li^+ transport through the electrolyte/SEI interface and through the SEI itself extensive simulations of model SEIs comprised of dilithium alkylcarbonates (ethylene and butylene) have been initiated using a new polarizable force field. The force field has been re-parameterized against higher-level quantum chemistry calculations and fit to accurately reproduce conformational properties of alkylcarbonates, electrostatic field around these molecules in vacuum, and molecular dipole moments. Specifically, simulations of the following systems and thermodynamic conditions are currently underway:

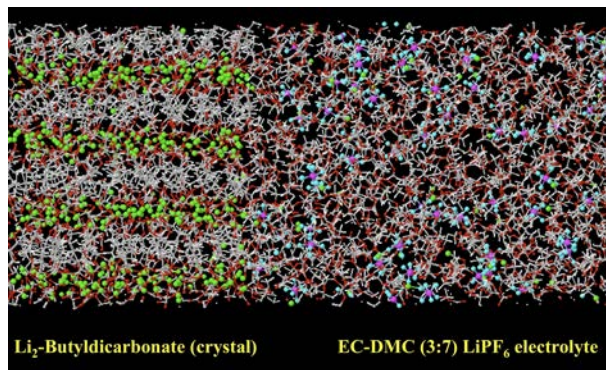


Figure 1. Snapshot from simulation of electrolyte/SEI (crystal) interface. Lithiums are green, oxygens –red, phosphorus –blue, carbons-grey.

1) *Amorphous phase of bulk Li_2 -ethylenedicarbonate, Li_2 -butylenedicarbonate, and their 50/50 mixture in the temperature range 363 to 500K.* These simulations will allow us to investigate the influence of SEI composition on mechanisms of Li^+ transport.

2) *Crystal phase of bulk Li_2 -ethylenedicarbonate, Li_2 -butylenedicarbonate in the temperature range 363-500K.* These simulations will allow us to compare mechanisms of Li^+ transport in amorphous and ordered SEI regions comprised of alkylcarbonates. Since crystallization temperature of alkylcarbonates is relatively high, the presence of crystalline or semicrystalline regions of these compounds is likely in the SEI layers. Our preliminary results indicate that at 393K Li^+ transport through carbonate/ Li^+ -rich layers (see Fig. 1) is faster than in the amorphous phase at the same temperature.

3) *Electrolyte/SEI interfaces.* Systems comprised of EC-DMC(3:7) LiPF_6 electrolyte and model SEI layers (crystal and amorphous) discussed in 1 and 2 are being simulated in order to study structure and dynamics at the interface between electrolyte and alkylcarbonate SEIs as well as mechanisms and interfacial resistance for of Li^+ translocation from electrolyte into SEI. A snapshot of such a system is shown in Fig. 1.

4) *SEI self-assembly in electrolyte.* The earlier stages of formation of outer SEI through aggregation of alkyl carbonate compounds in the electrolyte are also being investigated. In these simulations, Li_2 -alkyldicarbonates were dispersed in EC-DMC(3:7) LiPF_6 electrolyte using a biasing repulsive potential. Then, the biasing potential was switched off and evolution of SEI self-assembly was investigated. Of interest is the structure of the resulting SEI and the amount of salt (LiPF_6) present in the SEI.

TASK 3.4 - PI, INSTITUTION: Khalil Amine and Larry Curtiss, Argonne National Laboratory

TASK TITLE - PROJECT: Electrolytes – Advanced Electrolyte and Electrolyte Additives

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Safety, cycle/calendar life, and abuse tolerance

OBJECTIVES: Develop an Advanced Quantum Model to predict functional additives that form stable SEI on carbon anodes and cathodes. Expand model to predict how additives interact with the surface of anode and cathode during initial charging. Synthesize suitable additives predicted by model, characterize and perform extensive cycle and calendar life tests.

GENERAL APPROACH: Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings. Use density functional studies of graphite surface reactions to determine mechanisms for protective film formation from additives.

STATUS OCT 1, 2010: Completed the first phase development of state-of-the-art quantum chemical models to assist in the screening of potential additive candidates by predicting their oxidation and reduction potentials. Initiated refinement of the model and theoretically screened over 100 potential additive molecules.

STATUS SEP. 30, 2010: The promising additive candidates obtained from screening will be further investigated computationally for decomposition products that form a SEI, and testing will be initiated on their performance in a full cell configuration.

RELEVANT USABC GOALS: 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:

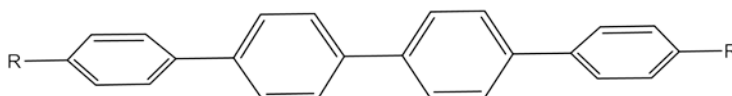
- (a) Investigate decomposition pathways for the promising additive candidates identified through reduction potential screening and recommend ones for experimental testing. (Apr. 11) **Complete**
- (b) Experimental testing of carbonate-based additive candidates predicted from our computational model. (May 11) **Complete**
- (c) Apply our quantum chemical model for calculation of the oxidation potentials of redox shuttles to predict candidates for experimental testing. (Jul. 11) **Complete**
- (d) Calculate structures of SEI components involving carbonates for identification in experimental studies. (Sep. 11) **Delayed, due Nov. 11**
- (e) Carry out quantum chemical studies of feasibility of reaction pathways for polymerization of electrolyte salts. (Sep 11) **Complete**

PROGRESS TOWARD MILESTONES

Our approach for the development of new electrolyte additives for SEI formation involves screening of reduction potentials through the use of accurate density functional methods followed by investigation of the mechanism of decomposition through an investigation of reaction pathways. Finally the theoretical results are related to the performance of the additives in a battery cell. A good solid electrolyte interphase (SEI) prevents further electrolysis of the electrolyte and increases battery cycle life. Our database of additives has increased to over 350 species. All have been screened for reduction potentials and some further studied for decomposition pathways to form SEI components. Among those additional species screened have been more than 50 new, potential battery additives including dioxathiolanes, sultones, imidazoles, isocyanates, diazines, triazines, diazoles, triazoles, piperazines and piperidines. Many have acceptable reduction potentials for battery additives.

Density functional theory (DFT) has been used to investigate redox shuttle molecules that can be reversibly oxidized and reduced at specific redox potentials to prevent dangerous electrical overcharge in Li-ion batteries. Potential shuttles must work with high energy density electrodes and be compatible with Li-ion chemistries.

A series of 13 substituted quaterphenyls were examined. The t-butyl derivative has been synthesized and has an oxidation potential of 4.4 to 4.5 V but limited solubility in the Gen2 carbonate electrolyte. Calculated free energies of solvation for the quaterphenyls ranged from 9.9 kcal/mol for t-butyl to 26.1 kcal/mol for $P(=O)(CH_3)_2$.



Additional testing of the 1,3,5-triallyl-[1,3,5]triazinane-2,4,6-trione (TTT), which theory indicated to be a promising SEI additive was carried out. Figure 1 is the differential capacity profiles of the cells with no and 1w% TTT. No perceptible difference could be observed. In terms of capacity retention evaluations, various concentrations of TTT were used to find the optimized condition. With 0.2 w% additive, the cell showed dramatic improvements in capacity retention, from 28% capacity loss of the control electrolyte to 15% capacity loss with 0.2 w% TTT at 55°C. In addition, by using a small amount of TTT, the impedance effect can be controlled. As shown in Fig 2, 0.2 w% of TTT did not significantly increase the impedance of the cell system, which can be very favorable to high power applications of Li-ion batteries.

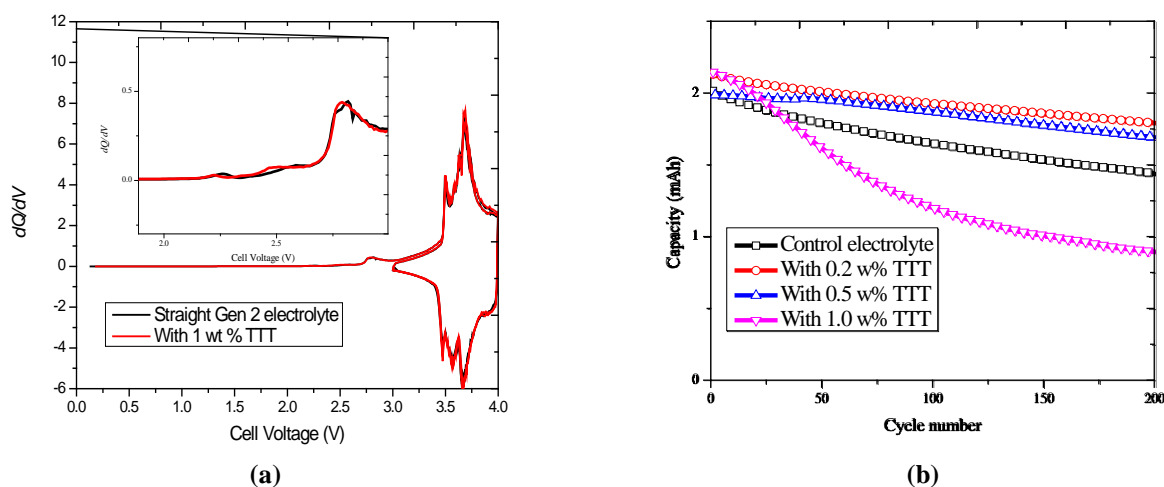


Figure 1. (a) Differential capacity profiles of MCMB/NCM cells, electrolyte: 1.2M $LiPF_6$ EC/EMC 3/7+1% TTT; (b) Capacity retention of MCMB/NCM cells cycled between 3 and 4.0V at 55 °C in electrolyte of 1.2M $LiPF_6$ EC/EMC 3/7 with no and various amounts of the additive TTT.

TASK 3.5 - PI, INSTITUTION: Brett Lucht, University of Rhode Island

TASK TITLE - PROJECT: Electrolytes – Development of Electrolytes for Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cell performance, life, cost: Calendar life: 40°C, 15 yrs; Survival Temp Range: -46 to +66°C; Unassisted Operating & Charging Temperature Range, -30 to +52°C.

OBJECTIVES: Develop novel electrolytes with superior performance to state-of-the art (LiPF₆). Develop additives that allow for formation of protective coatings on the cathode, *i.e.*, a cathode SEI, and enhance electrochemical stability above 4.5 V. Develop electrolytes for improved performance of Si-based alloy anodes.

GENERAL APPROACH: Investigate properties of LiPF₄C₂O₄/carbonate electrolytes in small Li-ion cells. Investigate electrode surface films for cells cycled with LiPF₄(C₂O₄) to determine source of performance differences. Investigate incorporation of electrolyte SEI forming additives for Si-based Alloy anodes. Investigate cathode film forming additives for high voltage (>4.5 V) cathode materials. Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation.

STATUS OCT. 1, 2010: Developed cathode film-forming additives that improve the cycling performance of graphite/LiNi_xCo_{1-2x}Mn_xO₂ cells cycled to high voltage (4.8 V vs. Li). The additives include organic and inorganic species. Expanded our investigation of the novel salt LiPF₄(C₂O₄) by testing it in coin cells under accelerated aging conditions with graphite/LiNi_xCo_{1-2x}Mn_xO₂ cells, and RT cycling of graphite/LiMn₂O₄ and graphite/LiFePO₄, and graphite/LiNi_xCo_{1-2x}Mn_xO₂ cells containing PC.

STATUS SEP. 30, 2011: Will develop additional cathode film-forming additives for high-voltage cathodes, investigate the low-temperature(-30°C) performance of LiPF₄(C₂O₄)/PC electrolytes after accelerated aging, develop an understanding of the source of initial capacity fade during formation cycling with LiPF₄(C₂O₄) electrolytes, and investigate novel electrolytes to improve performance of Si-based alloy anodes.

RELEVANT USABC GOALS: Calendar life: 40°C, 15 yrs; Survival temp. range: -46–52°C; Cold cranking power at -30°C; Cycle life; Peak Pulse Discharge Power, 10 sec.

MILESTONES:

- (a) Investigate cell performance upon accelerated aging of graphite/ LiNi_xCo_{1-2x}Mn_xO₂ cells with LiPF₄(C₂O₄)/PC electrolytes compared to LiPF₆ electrolytes. (Mar. 11) **Complete**
- (b) Develop improved cathode film forming additives for high-voltage Ni-Mn spinel cathode materials. (Jul. 11)**Complete**
- (c) Develop an understanding of the source of irreversible capacity loss with LiPF₄(C₂O₄) electrolytes during formation cycling. (Jul. 11)**Complete**
- (d) Investigate novel electrolytes to improve performance of Si-alloy anodes. (Sep. 11)**Complete**

PROGRESS TOWARD MILESTONES

Our expected status for September 30th, 2011 was achieved. Additional cathode film forming additives for high voltage cathodes have been developed. The low temperature performance of $\text{LiPF}_4(\text{C}_2\text{O}_4)/\text{PC}$ electrolytes after accelerated aging has been investigated. A strong understanding of the source of initial capacity fade during formation cycling with $\text{LiPF}_4(\text{C}_2\text{O}_4)$ electrolytes has been developed. Novel electrolytes were found that improve performance of Si anodes.

Milestone (a) was completed in our Q3 report and submitted for publication.

With regards to milestone (b): investigations of $\text{LiPF}_4(\text{C}_2\text{O}_4)$ in PC based electrolytes, cell cycling and post-mortem analysis of the electrodes has been completed. Cells containing $\text{LiPF}_4(\text{C}_2\text{O}_4)$ in PC/EMC have similar cycling performance at RT to cells containing LiPF_6 in EC/EMC or $\text{LiPF}_4(\text{C}_2\text{O}_4)$ in EC/EMC (Fig. 1). The initial cycling performance at low temperature (-10 C, charge and discharge) is better for the $\text{LiPF}_4(\text{C}_2\text{O}_4)$ electrolytes than the LiPF_6 electrolyte. The cells were then stored at 55°C for two weeks to simulate accelerated aging where cells containing LiPF_6 electrolytes surprisingly out performed cells containing $\text{LiPF}_4(\text{C}_2\text{O}_4)$ electrolytes. Further investigations of $\text{LiPF}_4(\text{C}_2\text{O}_4)$ electrolytes containing MB, with superior low temperature performance, and good thermal stability will be investigated in FY12.

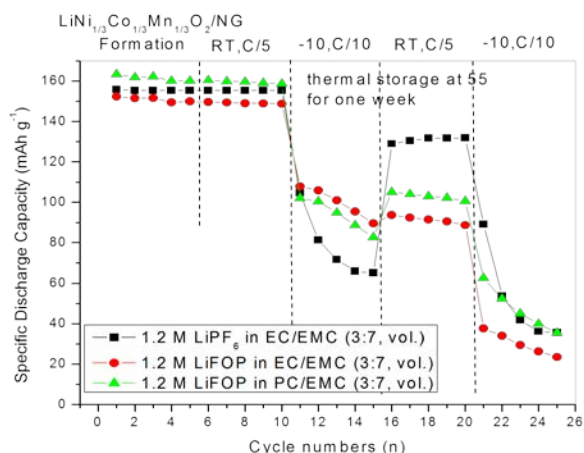


Figure 1. Cycling performance of graphite / $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cells with different electrolytes.

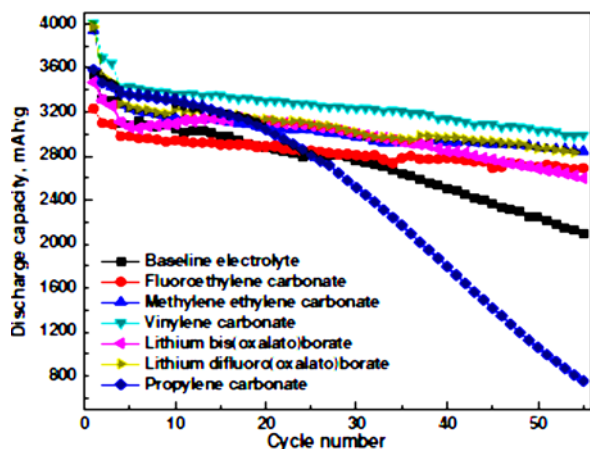


Figure 2. Cycling performance of Si/Li half cells containing various electrolytes.

With regards to milestone (c) the results were reported in our Q2 report.

With regards to milestone (d): Si anodes were cycled with LiPF_6 /carbonate electrolytes with various additives and post-mortem analysis conducted (Fig. 2). Several of the additive/electrolyte combinations provide superior cycling performance. The best additives include VC, MEC, and $\text{LiF}_2(\text{C}_2\text{O}_4)$. Surprisingly, cells containing FEC did not perform as well as other electrolytes. *Ex-situ* surface analysis suggests the cycling performance differences are due to differences in the structure of the Si anode SEI.

Collaborations Q4: M. Smart (NASA-JPL), V. Battaglia, R. Kostecki, J. Kerr (LBNL), P. Guduru (Brown Univ.) A. Garsuch (BASF), J. Zhang (PNNL).

TASK 3.6 - PI, INSTITUTION: Daniel Scherson and John Protasiewicz, Case Western Reserve University

TASK TITLE - PROJECT: Electrolytes – Bifunctional Electrolytes for Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Abuse tolerance

OBJECTIVES:**I.** Design, synthesize, and characterize physical, electrochemical, and interfacial characteristics of functionalized Li-salt anions containing: **a.** phosphorus moieties known to impart materials with flame retardant properties (Flame Retardant Ions or FRIONs); and **b.** additional functional redox active groups capable of providing overcharge protection, FROPs. These new classes of materials will improve device safety without impairing device performance. **II.** Develop and implement ATR-FTIR spectroscopic methods for monitoring *in situ* the nature of products generated at Li-ion battery anodes under highly-controlled conditions.

GENERAL APPROACH: **I.** Develop methods for the chemical functionalization of anions known to improve the performance of Li-ion batteries with covalently linked groups displaying flame retardant and/or overcharge protection attributes. **II.** Establish guidelines for the rational design and synthesis of optimized FRIONs and FROPs based on the analysis of results of testing in actual Li-ion batteries. **III.** Develop new *in situ* tactics for the application of attenuated total reflection Fourier transform infrared ATR-FTIR for the characterization of solution products generated at Li-ion battery anodes and solid electrolyte interfaces formed therein.

STATUS OCT. 1, 2010: Fully synthesized, purified and characterized first-generation LiBOP-type FRIONs in amounts sufficient for thorough battery testing. Synthesized and preliminarily evaluated several members of the cyclic borate phosphine oxides (CBPO)-type of FRIONs. Preliminary measurements with the newly constructed *in situ* ATR-FTIR cell aimed at monitoring *in situ* the composition of the electrolyte and surface films on ultrapure Li metal electrodeposited *in situ* in the same cell in alkyl carbonate solvent-salt formulations provided by Novolyte Technologies. Completion of flammability tests of first FRION. Submission of first paper to refereed Journal.

STATUS SEP. 30, 2011: Completion of synthesis, purification and characterization of CBPO, a second class of FRIONs, in amounts sufficient for full electrochemical and battery testing. Large scale synthesis and purification of first-class FRIONs for thorough performance assessment in Li-ion batteries. Systematic *in situ* ATR-FTIR spectroscopic studies involving solvent formulations incorporating Case FRIONs as additives.

RELEVANT USABC GOALS: No fire or rapid disassembly of cells during abuse conditions.

MILESTONES:

- (a) Prepare and fully characterize three new LiBOP-type FRIONs. (Oct. 10) **Complete**
- (b) Prepare and characterize new FRIONS based on properties of LiBOP-type FRIONs. (Aug. 11) **Delayed, due Oct. 11. Original plan modified. Materials in (a) did not prove useful. New FRIONS are scheduled to be prepared and characterized in 2012.**
- (c) Implement *in situ* ATR-FTIR cell and examine solution phase and SEI for electrolyte formulations with and without first type of FRIONs. (Aug. 11) **Delayed, due to technical issues.**
- (d) Synthesize and characterize completely new class of FRIONs (CBPOs). First example of CBPO will be achieved, and initial evaluation will be accomplished. (Aug. 11) **Complete**
- (e) Implement *in situ* ATR-FTIR cell and examine solution phase and SEI for electrolyte formulations with and without second type of FRIONs. (Sep. 11) **Delayed, due to technical issues.**

PROGRESS TOWARD MILESTONES

a. Synthesis and characterization of FRIONS – The flammability profiles of the three new Li salts of cyclic triol borates reported last quarter (see Scheme 1, where R = Me; R' = Ph, Me or R = Et; R' = Ph) were investigated using microcombustion calorimetry; the results are compiled in Table 1. As evidenced from the data therein, these new materials display a higher char yield as well as a slight decrease in the total heat released compared with previous salts. In addition to synthesizing approximately 30 grams of two lithium cyclic triol borates (R = Me, Et; R' = Ph) for additional testing, four new cyclic triol borate salts were synthesized (R = Me; R' = Cy, 4-CH₃Ph, OH and R = Et; R' = OH). Lastly, and particularly exciting, we have succeeded in synthesizing a material displaying features consistent with a lithium **bicyclic** borate phosphine oxide (Scheme 2, Fig. 1). This compound, for which the ³¹P NMR LiPB_{OH} (²J_{PH} = 6.6 Hz) is shown in Fig. 1, is structurally analogous to the cyclic triol borate salts, where R = Me, Et and R' = OH; and will provide an accurate measure of the impact the phosphine-oxide moiety has, not only on the flammability profile, but also on the electrochemistry of these **bicyclic** lithium salts.

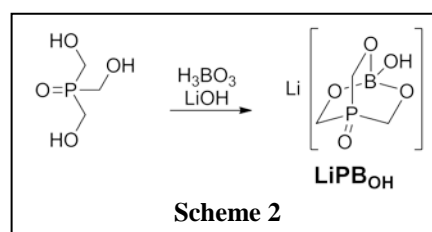
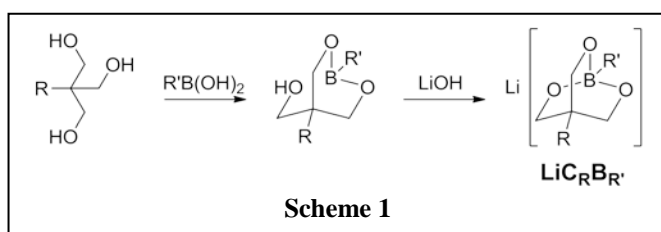
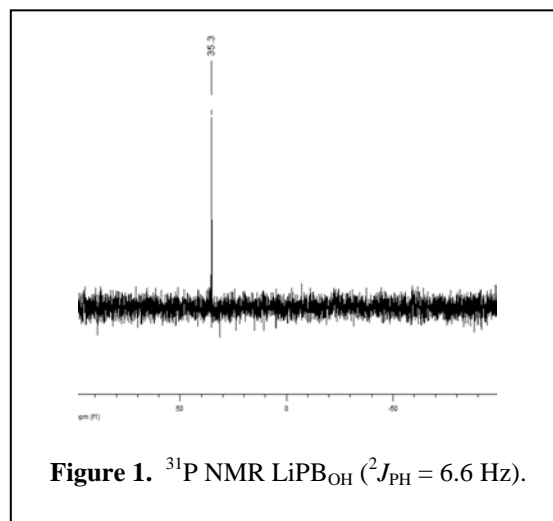


Table 1. Heat Release Data.

Compound	Mean Char Yield ^a (wt%)	Mean Total HR ^{ac} (kJ/mol)
LiC _{Me} B _{Me}	34.00(10.81)	18.1 (0.2)
LiC _{Me} B _{Ph}	30.74 (1.09)	21.1 (0.2)
LiC _{Et} B _{Ph}	31.53 (1.32)	19.61 (0.4)
LiBOBPHO-Ph	23.62 (0.4)	20.5 (0.5)
LiBOBPHO-Ar	20.15 (0.6)	24.7 (0.2)



b. In situ FTIR Measurements – Further refinements have been introduced to the acquisition and analysis of *real time* FTIR spectra in the external reflection mode (IRAS) using a CaF₂ window and *p*-polarized light to enhance surface spectral contributions. This new strategy enables both voltammetric and spectral data to be displayed simultaneously in real time allowing features associated with the two types of measurements to be correlated directly. Data were collected in 1M LiPF₆ in EC/EMC (3:7 by vol) with the Ni electrode pressed against the window while scanning the potential from the open circuit value (OCP ca. 2.2 V) down to 0.05 V vs. Li/Li⁺, yielding from run-to-run highly reproducible results.

TASK 3.7 - PI, INSTITUTION: Wesley Henderson, North Carolina State University

TASK TITLE - PROJECT: Electrolytes – Inexpensive, Nonfluorinated (or Partially-Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-cost cell materials, abuse tolerance, low-temperature performance

OBJECTIVES: Develop new anions as replacements for PF₆⁻ or as additives for electrolytes

GENERAL APPROACH: Synthesize and fully characterize two classes of nonfluorinated (or partially-fluorinated) anions: 1) chelated and non-chelated organoborate anions (related to bis(oxalate)borate (BOB⁻)), and 2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both Li salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical, and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as LiPF₆ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion.

STATUS OCT. 1, 2010: New salts based upon organoborate and Hückel-type anions were prepared and some of these have been scaled up for extensive characterization. Ionic liquids also were prepared from these anions, and characterized. The phase behavior and properties of solvent-LiBOB and -LiBF₄ mixtures were determined for comparison with the new salts to aid in understanding the widely-varying solubility noted for these salts.

STATUS SEP. 30, 2011: Partially-fluorinated anions will have been prepared for comparison with the nonfluorinated salts. These will consist of both fluorine and cyano electron-withdrawing components. The work exploring the solubility and Li⁺ cation coordination of organoborate anions in aprotic solvents will provide insight into the selection of these salts as additives to electrolytes.

RELEVANT USABC GOALS: Available energy: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); cycle life: 5000 cycles (10 mile) and 3000 cycles (40 mile); calendar life: 15 years (at 35°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:

(a) Characterize the electrochemical properties of lithium dicyanotriazolate (LiDCTA). (Apr. 11)

Delayed to Apr. 12

(b) Synthesize and purify partially-fluorinated cyanocarbanions. (Apr. 11) **Complete**

(c) Characterize partially-fluorinated cyanocarbanions. (Sep. 11) **Delayed, due Jan. 12**

(d) Synthesize, purify, and characterize cyanocarbodianions. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Characterization of LiDCTA: Work was delayed by difficulties associated with the synthesis and impurities in the salt. Characterization work is therefore ongoing.

Anion Synthesis: The synthesis of several new anions (DCP^- and ETAC^-) is being scaled up to facilitate full-scale testing of the anions in electrolytes (Fig. 1). Other dianion salts are also in preparation. The DCP^- and TCP^{2-} anions were prepared as potassium salts and issues have been found with regard to the subsequent full lithiation of these salts. Purification of the new salts to electrochemical-grade materials is therefore a current focus. The anions containing cyano groups are found to polymerize during thermal degradation (Fig. 2) forming black polymers. This is one useful feature of cyano-containing materials which may serve as a useful shut-down mechanism for a battery during thermal abuse. Unfortunately, the TCP^{2-} salts have been found to have poor solubility in aprotic solvents. Crystal structures for the pure LiETAC (Fig. 3) and a $(\text{THF})_1\text{:LiETAC}$ solvate have been determined to gain insight into how this anion coordinates Li^+ cations. The electrochemical properties of the salts in aprotic solvent mixtures are currently being determined.

Concentrated Ionic Liquid (IL)-Based Electrolytes: Highly concentrated IL- LiX -solvent mixtures (high concentration of LiX) have been prepared with select amounts of solvent so that little or no bulk solvent is present in the electrolytes. These mixtures have been characterized and are now being tested as electrolytes with various electrode materials.

Collaborations: Oleg Borodin and Richard Jow (Army Research Laboratory) and Stefano Passerini (Münster Electrochemical Energy Technology group, University of Münster).

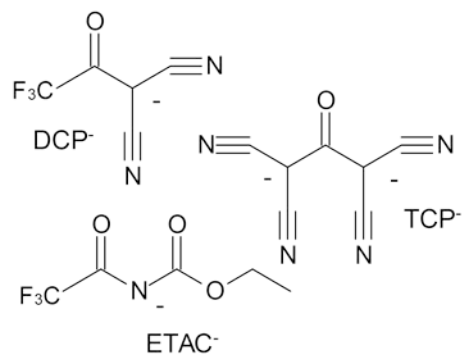


Figure 1. Examples of anions synthesized.

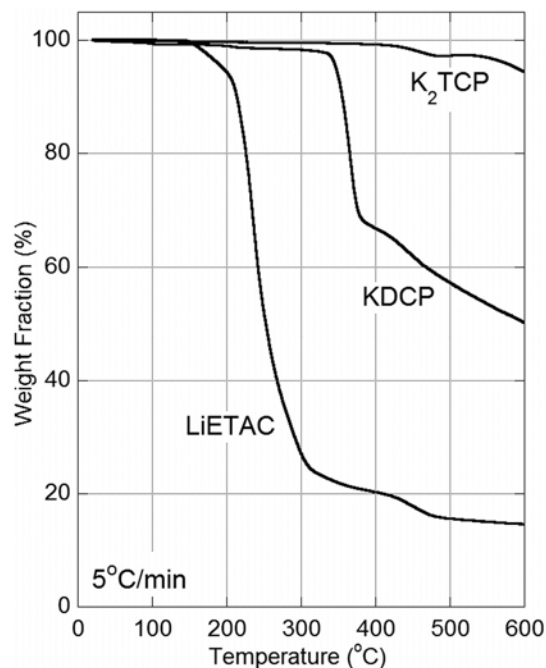


Figure 2. TGA heating traces of the salts.

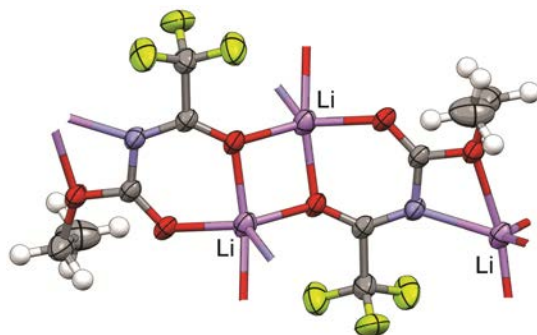


Figure 3. Ion coordination in the crystal structure of LiETAC (Li-purple, O-red, N-blue, F-green).

TASK 3.8 - PI, INSTITUTION: C. Austen Angell, Arizona State University

TASK TITLE - PROJECT: Electrolytes – Sulfones with Additives as Electrolytes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor abuse tolerance, low energy density, and improved safety.

OBJECTIVES: To devise new electrolyte solvent chemistries that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection, and to provide optimized nanoporous supporting membrane for this electrolyte.

GENERAL APPROACH: (i) Design new solvent molecules and solvent mixtures that retain the high-oxidation resistance already demonstrated for noncyclic sulfones while maintaining the solubility of LiPF₆ and lowering the liquid viscosity. Included is the determination of how cosolvents will act with ethylmethyl sulfone (EMS) to produce the same effect for mixtures with EMS. (ii) Employ new design principles involving “Maxwell slats” to synthesize nanoporous supports optimized to contain the electrolytes with minimum electrode separation for maximum conductance.

STATUS OCT 1, 2010: Commercially-available methyl sulfonyl fluoride was evaluated, and found uninteresting as a single solvent (because of poor solubility of LiPF₆), interesting as a cosolvent with EMS based on conductivity (factor of 3 more conductive than with pure EMS as solvent), but inadequate based on oxidative stability. Likewise for methane sulfonyl chloride which had previously been studied as a single solvent and found to have a wide “window”. The latter case has been instructive to demonstrate the lack of synergism of EMS with cosolvents. Where initial experience suggested all co-solvents might experience enhanced stability deriving from the presence of the sulfone, this case proves that it is NOT general, implying that studies of its origin when it occurs, will be desirable. Attempts were made to fluorinate one or more of the ring methylene groups on the known wide window, electrolyte solvent tetramethylene sulfone (sulfolane), for which a substantially-reduced viscosity is predicted.

STATUS SEP. 30, 2011: A substantial number of EMS + cosolvent systems will have been examined, and their LiPF₆ dissolving capacities determined, their electrical conductivities examined, and their electrochemical stabilities evaluated. A series of fluorination studies, tested in button cells, will have been carried out and the more promising routes refined. New types of supporting polymers will have been examined and compared with standard cases. These polymer supports will also have been tested for their sequestering abilities with sulfur as a cathode material in Li-S cells and evaluated for their ability to withstand polysulfide components in the solution.

RELEVANT USABC GOALS: 1000 cycles (80% DoD); 10 year life. An electrolyte with electrochemical window 5.2 volts and conductivity 20 mS/cm.

MILESTONES:

- (a) Complete full evaluation of cosolvent systems and determine useful limits. (Dec. 10)**Complete**
- (b) Realize first two fluorination objectives or prove inaccessible. (Mar. 11)**Complete**
- (c) Perform preliminary evaluation of “Maxwell slat” nanoporous membrane concept Mar. 11**Complete –more advanced evaluations have been carried out and have succeeded.**
- (d) Perform advanced evaluation of “Maxwell slat” concept for creation of self-supporting films of nanoporous supporting membrane for sulfone electrolytes. Perform preliminary tests of this medium for isolation of polysulfides in Li-S cells. (Jul. 11)**On-going, due Jul. 12**
- (e) Realize second two fluorination prospects, or prove them inaccessible. (Jul. 11)**Complete**

PROGRESS TOWARD MILESTONES

1. Sulfone solvent electrolytes. Following the success in using mixed solvent sulfones with LiPF_6 electrolyte to intercalate graphite anodes reversibly, attention was focused on the cycling propensity at the high voltage $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathode. With the cathodes we have fabricated we can cycle many times (>50 cycles) without failure but have been unable to obtain full capacity due to some irreversible process occurring above 4.7V. The high intrinsic stability of sulfones is not realized here. Further tests will be made when “standard” cathodes become available.

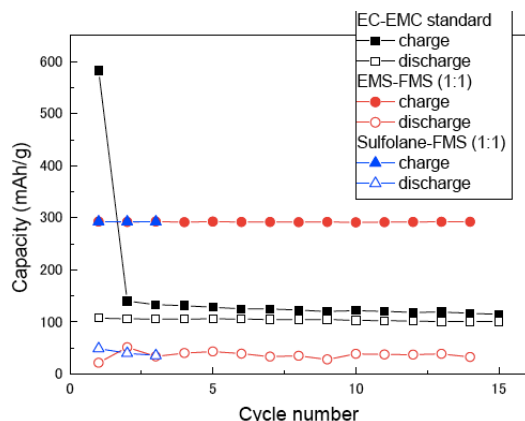


Figure 1. Specific charge/discharge capacities for the half-cell EMS-FMS- $\text{LiPF}_6(1\text{M})$ $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, conducted at C/5 rate, compared with other electrolytes.

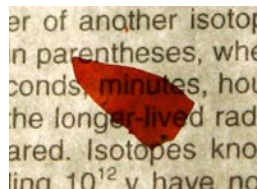


Figure 2. Sample of cresol-solubilized nanoporous net, formed using tetrahedral Ti (IV) center and bis-phenol A linker.

2. Nanoporous film separators. After months of effort in preparing what were expected to be simple, self-assembling, nanoporous films, based on an aqueous hydrogen bonding protocol used with great success in the making of nanoscopic models from DNA strands by colleague Hao Yan (Science cover, April 15, 2011), the hydrogen bonded model has been abandoned in favor of a covalent model with which more severe problems were expected. Fortunately, success has been almost immediate. A powder obtained by eliminating acetic acid from $\text{Ti}(\text{OEt})_4$ and bis-phenol A (epoxy-resin precursor) has been found to be soluble in cresol, and the viscous solution dries to a flexible film, shown in Figure 2. The cresol occupies the pores but can then be removed by methanol extraction and drying, see Figure 3 (RHS). The amorphous XRD patterns are shown in Figure 3, LHS. Efforts are now under way to control the pore size and to fill the pores with ambient temperature lithium ion conductors like LiAl_2Cl_7 - LiSO_3Cl “ionic oil” ($\sigma(25^\circ\text{C}) \sim 10\text{mS/cm}$) and higher voltage-stable analogs.

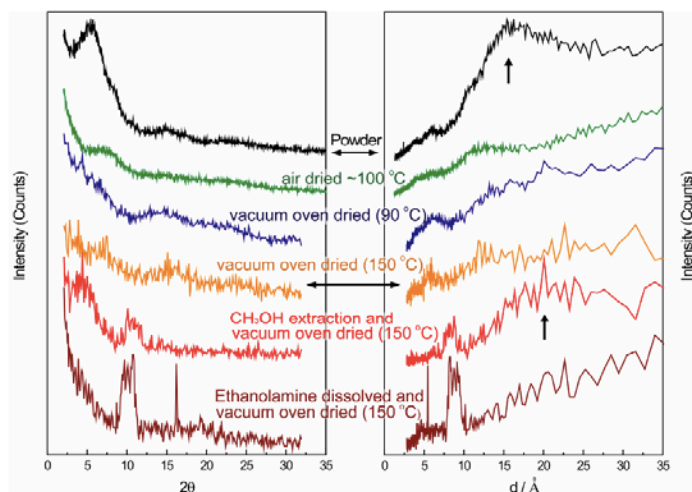


Figure 3. XRD and pore separation patterns for nanoporous net. **LH panel** (top down) XRD for the initial reaction product (powder) showing larger small angle peaks from pore-pore correlations: the film of Fig. 2 (air-dried) and others, as labeled. Most significant is the 5th pattern, obtained from the film of Fig. 2 after solvent extraction of the cresol by methanol and vacuum drying, showing restoration of the pore-pore scattering. **RH panel.** Conversion of XRD to pore separation distance, $d = 1/2pQ$, suggesting the presence of 15-20Å pores.

3. Superionic conducting vitreous state separators. In a new branch of this program, glassy state conductors with wide “windows” and reduced side reactions are now also being explored.

BATT TASK 4

CATHODES

Task 4.1 - PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE - PROJECT: Cathodes – Novel Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, cost, and abuse tolerance limitations of Li-ion batteries

OBJECTIVE: To develop low-cost, high-energy and high-power Mn-oxide-based cathodes.

GENERAL APPROACH: Structurally-integrated $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ composite structures (M = Mn, Ni and Co) provide exceptionally high-rechargeable capacities (>200 mAh/g) if charged above 4.5 V, which destabilizes the electrode surface, resulting in a first-cycle irreversible capacity loss. Our approach is to design surface architectures that mitigate these performance limitations. In FY2011, we will continue our efforts to 1) stabilize the electrodes at high potentials without compromising rate capability, 2) minimize the need for electrochemical activation, 3) evaluate autogenic reactions to fabricate carbon, metal-oxide, and metal-phosphate coatings, and 4) use atomic simulations to model structural configurations of surface-protected LiMn_2O_4 electrodes.

STATUS OCT 1, 2010: Progress was made in enhancing the rate capability of high-capacity $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ (M=Mn, Ni, Co) electrodes by stabilizing the electrode surface with a lithium-nickel-phosphate coating. Autogenic reactions were successfully used to synthesize and carbon-coat LiFePO_4 in a single step. Theoretical studies of the solubility and surface structure of LiMn_2O_4 in an acidic medium were extended and completed.

STATUS SEP. 30, 2011: Progress will have been made in enhancing the surface stability of 'layered-layered' $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes at high potentials, with improvements in rate capability and cycle life. Methods to overcome the first-cycle capacity loss by minimizing the necessity for electrochemical activation will have been evaluated. Attempts to deposit carbon and stabilizing metal oxide or metal phosphate stabilizing layers on metal oxide electrode surfaces by autogenic reactions will have been made. Theoretical simulations of coated electrode surfaces will have been conducted.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:

- (a) Engineer, improve, and evaluate the electrochemical properties of stabilized surfaces of composite electrode structures with a high Mn content. (Sep. 11)**Complete**
- (b) Evaluate autogenic processes for coating metal oxide cathode particles with carbon and for fabricating stabilized surfaces with metal oxide and/or phosphate layers. (Sep. 11)**Complete**
- (c) Model coatings and interfacial phenomena at the surface of LiMn_2O_4 electrodes. (Sep. 11)**Complete**

PROGRESS TOWARD MILESTONES

Collaborators: J.R. Croy, M. Balasubramanian, S.-H. Kang, K. Gallagher, D. Kim

Milestone (a) addressed: Engineer, improve and evaluate the electrochemical properties and surface stability of composite electrode structures with a high Mn content.

Li_2MnO_3 -stabilized electrodes with composite structures, notably, ‘layered-layered’ $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ (e.g., $M = \text{Mn}, \text{Ni}, \text{and Co}$) materials, are currently receiving worldwide attention because of their ability to deliver capacities of 250 mAh/g or more, when electrochemically activated at approximately 4.6 V. The electrochemical activation process damages the rate capability of the electrode; this damage can, however, be mitigated to some extent by surface protection of the electrode particles prior to activation. Furthermore, when charged to this high potential, composite electrode materials with a high Mn content tend to undergo voltage decay on continuous cycling, thereby lowering the energy and power output of the cell. Studies were initiated in 2011 to address and understand this issue [1, 2].

In particular, advantage was taken of the element specific nature of XAS to elucidate the chemical and structural details of a surface treatment intended for the protection of high-capacity cathode materials. Electrochemical data, described in an earlier report, have shown that surface treatments of $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiMO}_2$ ($M = \text{Mn}, \text{Ni}, \text{Co}$) cathodes with an acidic solution of lithium-nickel-phosphate (LNP) improves their capacity, rate, and cycling stability. XAS data revealed that the surface treatment of $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiCoO}_2$ (LCMO) resulted in a modification of the composite structure itself, where Ni^{2+} cations, intended to be present in a LNP coating, instead displaced Li in the transition metal layers of the Li_2MnO_3 -like domains within the $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiCoO}_2$ structure (Fig.1(a-c)). X-ray diffraction data showed the presence of Li_3PO_4 , suggesting that phosphate ions in the acidic solution were responsible for Li extraction and Ni insertion with the formation of vacancies and/or Mn reduction for charge compensation. Furthermore, the above effects are not limited to LNP treatments. The results are consistent with a novel approach for synthesizing and tailoring the structures of high-capacity cathode materials whereby a Li_2MnO_3 framework is used as a precursor for synthesizing a wide variety of composite metal oxide insertion electrodes for Li-ion battery applications [1].

All the proposed 2011 milestones for this project have been met.

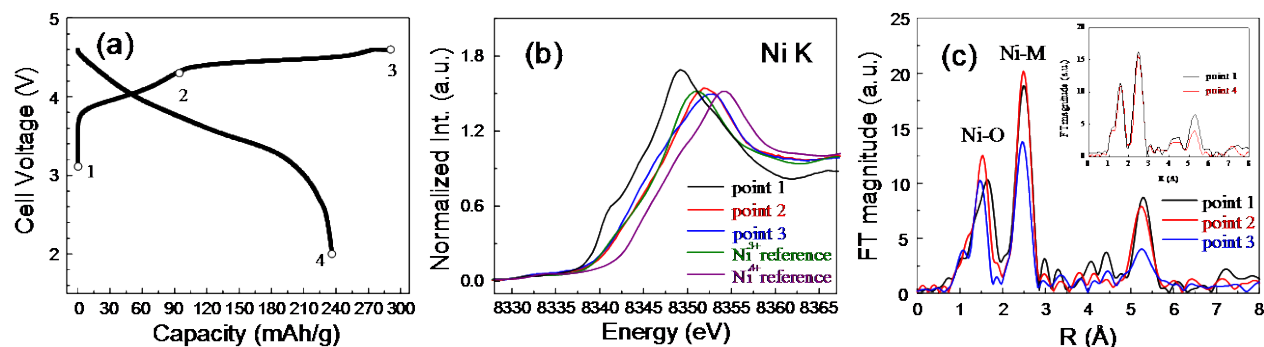


Figure 1. (a) Charge/discharge curve (4.6-2.0 V, 15 mA/g) for a Li/LNP-treated LCMO cell. The points indicate states of charge for XAS measurements; (b) Ni K-edge XANES at points 1, 2 and 3, against Ni^{3+} and Ni^{2+} references; and (c) FT data of electrodes at points 1, 2, and 3; the inset compares points 1 and 4.

References

1. J. R. Croy, S.-H. Kang, M. Balasubramanian and M. M. Thackeray, *Electrochem. Comm.* **13**, 1063 (2011).
2. J. R. Croy, M. Balasubramanian, S.-H. Kang, D. Kim and M. M. Thackeray, *Chem. Mater.* (2011). Submitted.

TASK 4.2 - PI, INSTITUTION: M. Stanley Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes - Materials – Novel Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg (700-800 Wh/kg), and (b) moderate-rate PHEV compatible cathodes, both of which are based on environmentally-benign materials.

GENERAL APPROACH: Our cathode approach is to place emphasis on low cost oxides and phosphates, both pure and modified with other transition metals, using a range of practical synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2010: For the LiFePO₄ olivine, it was determined that the rate capability can be improved by substituting *ca.* 5% of another ion such as vanadium or magnesium. This is believed to be due to a reduction of the nucleation energy for formation of the second phase. Such substitution also substantially enhances the volumetric capacity, by minimizing the amount of carbon conductor. It was also shown that the olivines can be formed hydrothermally. For the layered metal dioxides, we have determined that they can be structurally stabilized with around 3% Ni in the Li layer, that no more than 20% Co is required to achieve optimum capacity at rates exceeding 2C, and that charging potentials in excess of 4.3 V are required to achieve discharge capacities exceeding 200 Wh/kg. Candidate materials that allow for more than one electron reduction per transition metal were identified.

- LiFePO₄: > 120 Ah/kg for 100 cycles at 1 mA/cm² (1C rate).
- Layered Li_xCo_zNi_yMn_{1-y-z}O₂: 160 Ah/kg and 150 Ah/kg for 60 cycles at 1 and 2 mA/cm² respectively.

STATUS SEP. 30, 2011: For low-cost Li-Ion cells, we expect to identify the Li_xMn_{1-y-z}Ni_yCo_zO₂ systems that have the potential to achieve over 200 Ah/kg at a C rate. Emphasis will be placed on the Li_xMn_{0.4}Ni_{0.4}Co_yMn_{0.2-y}O₂ compositions. We will have extended our studies beyond olivine-structured lithium-metal phosphate and evaluated some manganese-containing iron phosphates (non-olivine). We also will have explored some higher-capacity, next-generation cathodes, including some based on vanadium.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, and lower cost batteries.

MILESTONES:

- (a) Identify LiNi_yMn_yCo_{1-2y}O₂ systems that can achieve 200 Ah/kg for PHEV applications. (Mar. 11) **Complete**
- (b) Identify and evaluate phosphate structures, containing Fe and/or Mn that have the potential of achieving an energy density exceeding 700 Wh/kg. (Sep. 11) **Complete**
- (c) Identify other materials, including those containing vanadium, that can undergo more than one electron transfer per redox center (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

The expected status was achieved, except that 200 Ah/kg was not achieved in NMC at C rate, except in the Li-rich materials where stability issues were identified.

Milestone (a) – Layered Metal Oxides is now complete. Our conclusion is that the composition $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ offers the best energy for rates up to at least 2C. For higher rates $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ is preferable. Although the Li-rich compounds, $\text{Li}_{1.2}\text{M}_{0.8}\text{O}_2$, can give higher capacities at low rates, C/10, at 21°C, their capacities fall to less than those of the Li/M = 1 compounds at the C to 2C rate. They also appear to release more heat and at a much lower temperature than the Li/M = 1 compounds (Fig. 1), although this can be improved by Al substitution. We have not investigated whether coatings will stabilize the structure.

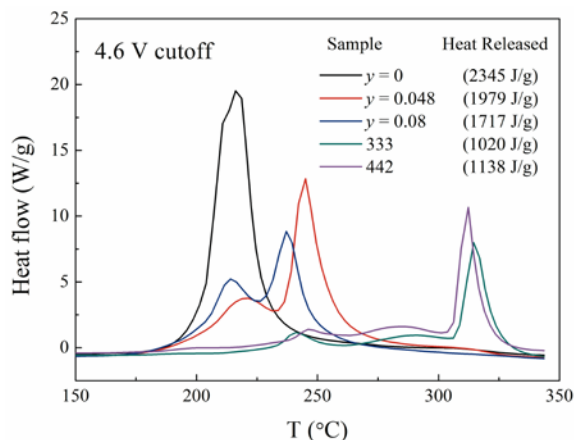


Figure 1. Differential scanning calorimetry at 10 °/min of delithiated $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08-y}\text{Al}_y\text{O}_2$ ($y = 0, 0.048, 0.08$) compared with the more stable NMC electrodes, $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ and $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$.

Milestone (b) - Lithium Iron-Containing Pyrophosphates. The last quarter, the student spent one month at Monash University and CSIRO in Melbourne investigating the use of ionic liquids as possible electrolytes for the 5 volt cathode, $\text{Li}_2\text{FeP}_2\text{O}_7$. None of the electrolytes proved to be stable, but a number of alternative compositions were proposed and we are following up on those. This system has the capability of attaining the 700 Wh/kg goal. The related $\text{Li}_2\text{CoP}_2\text{O}_7$ compound has been synthesized and characterized structurally.

Milestone (c) – Other Multi-electron Systems. Vanadium phosphates have been identified as the most promising class of materials for multi-electron redox amongst intercalation electrodes and the group has begun characterizing them.

Milestone (a) was a collaboration with Dr. Dillon's group at NREL. Milestones (b) and (c) are a continuing collaboration with Primet in Ithaca, the Ceder group at MIT, and several electrolyte groups, including PNL, ARL and CSIRO/Stony Brook.

The student working on the layered oxides has completed his thesis, and is now a postdoc at MIT.

Publications in 2011

1. H. Zhou, S. Upreti, N.A. Chernova, G. Hautier, G. Ceder, and M.S. Whittingham "Iron and Manganese Pyrophosphates as Cathodes for Lithium Ion Batteries," *Chemistry of Materials*, **23**, 293 (2011).
2. C. Ban, Z. Li, Z. Wu, M.J. Kirkham, L. Chen, Y.S. Jung, E.A. Payzant, Y. Yan, M.S. Whittingham, and A.C. Dillon, "Extremely Durable High-Rate Capability of a $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ Cathode Enabled by Single-Wall Carbon Nanotubes," *Advanced Energy Materials*, **1**, 58 (2011).
3. Z. Li, N. A. Chernova, M. Roppolo, S. Upreti, C. Petersburg, F.M. Alamgir, and M.S. Whittingham, "Comparative study of the capacity and rate capability of $\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ ($y=0.5, 0.45, 0.4, 0.33$)," *J. Electrochem. Soc.*, **158**, A516 (2011).

TASK 4.3 - PI, INSTITUTION: Marca Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes – Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, power and/or energy density, cycle life

OBJECTIVES: To develop low-cost benign cathode materials having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the USABC goals.

GENERAL APPROACH: Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties. Some work is directed towards surveying new materials with potential for increased energy density.

STATUS OCT 1, 2010: Electrochemical characterization of the Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O₂ (992) system was carried out this year. Aluminum substitution had little negative impact on the practical capacity and better cycling was achieved than for unsubstituted compounds, but no rate enhancement effect was observed. A systematic investigation of the effect of Ti substitution for Co in NMCs continues. Ti-substituted materials have increased electrochemical capacity compared to the unsubstituted compounds, but the mechanism remains unclear. A spray pyrolysis setup for synthesis of metal oxides and polyanionic composites with carbon has been optimized.

STATUS SEP. 30, 2011: Further investigations into the effect of Ti and Al substitution on NMCs will be carried out. This includes electrochemical and structural characterization in conjunction with other members of the BATT program (Cabana, Persson, Richardson, Chen). The spray pyrolysis system will be modified so that smaller particles can be produced.

RELEVANT USABC GOALS: High power, low cost (HEV). High energy, low cost, cycle life (EV, PHEV).

MILESTONES:

- (a) Complete structural and electrochemical characterization of Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O₂ system. (Jun. 11)**Complete**
- (b) Finish survey of Ti-substituted NMCs and select most promising materials for further study. (Jun. 11)**Complete**
- (c) Decrease particle size of polyanionic compound/C composites prepared by spray pyrolysis. Investigate synthesis of new materials by this method and others for comparison. (Sep. 11)**Delayed, due Sep. 12**

PROGRESS TOWARD MILESTONES

a) **Complete.** Work on the $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{Mn}_{0.45}]\text{O}_2$ system is now complete, and papers are being prepared. Analysis of high-resolution XRD data obtained at the APS showed that the $y=0.1$ material has a monoclinic distortion, while the $y=0$ and 0.05 compounds have the usual $R3_m$ symmetry. In the pristine state, all compounds contain 9-10% Ni_{Li} antisite defects, which decrease to 8.4% upon cycling. The monoclinic distortion in the $y=0.1$ material remains during cycling.

b) **Complete.** Neutron diffraction experiments on several Ti-substituted NMCs were carried out at the Los Alamos Neutron Science Center and results are currently being analyzed.

c) **On-going, due Sep. 2012.** Optimization of the spray pyrolysis synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is underway. It was found that loss of Li during the process resulted in products having some Ni in 8a (Li) sites. These ion-mixed compounds showed poor electrochemical performance. Loss of Ni can also occur during spray pyrolysis and results in products with a high Mn^{3+} content and reduced capacity at 4.7V vs. Li. Addition of 5% excess Li and Ni to the precursor solutions compensated for these losses and resulted in less defective materials with good electrochemical characteristics. The effect of the post-heat treatment on the morphology and electrochemistry of spray-pyrolyzed samples was studied and is shown in Fig. 1. A spray-pyrolyzed batch consisting of particles approximately 10 μm in diameter was divided in half. One half was heated to 900°C for fifteen minutes and yielded spherical particles consisting of large (1 μm) primary particles (shown in the inset on the left). The second half was heated to 700°C (right, inset) and yielded particles with a smooth texture. The XRD patterns and electrochemical characteristics of both materials were consistent with a disordered structure (Fd3_m), but far higher coulombic inefficiencies were observed for the fine-grained material. The higher surface area of this material resulted in greater reactivity with the electrolyte.

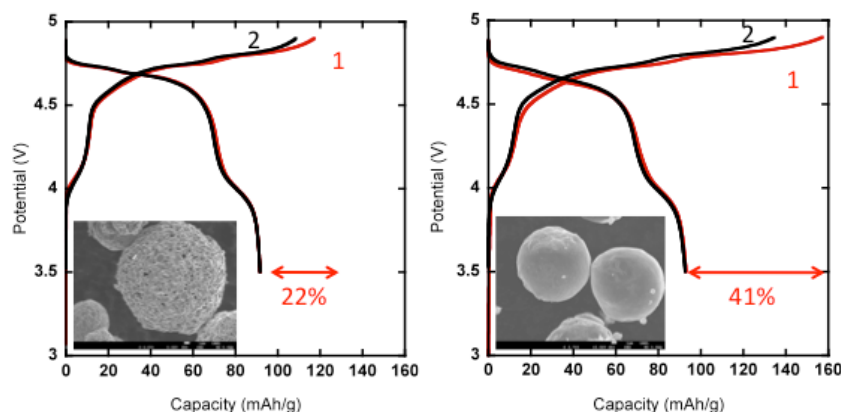


Figure 1. (left) Spray pyrolyzed $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ heated to 900°C for 15 minutes and (right) heated to 700°C for twelve hours.

Collaborations: J. Cabana-Jimenez, G. Chen, LNMS discussion group.

Presentation:

“Lithium Ion Battery Cathodes for Traction Applications” Marca M. Doeff, Electrical Energy Storage Meeting, University of Michigan, Ann Arbor, MI, August 3, 2011.

TASK 4.4 - PI, INSTITUTION: Arumugam Manthiram, The University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – High-Performance Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, energy density, power density, cycle life, and safety

OBJECTIVES: To develop (i) low-cost spinel oxide compositions that can offer high energy and power, excellent cycle life, good storage characteristics, and good safety, and (ii) low-cost cathodes based on polyanions that can offer a combination of high energy and power with excellent thermal stability and safety.

GENERAL APPROACH: Our approach is to continue to develop a firm scientific understanding of the factors that control/influence the electrochemical performances of the cathodes and utilize the knowledge gained to design and develop high-performance spinel and polyanion-containing cathode compositions. In this regard, (i) cationic and anionic substitutions and surface modifications of spinel oxide cathodes, and (ii) novel cathodes consisting of polyanions are being pursued. Particularly, (i) self-segregation of certain substituted cations to the surface during the synthesis process that can suppress metal ion dissolution from the cathodes and/or control the SEI layer formation in high voltage (~ 4.7 V) spinel cathodes and (ii) novel synthesis approaches for polyanion-containing cathodes are investigated. Conventional ceramic synthesis and innovative synthesis approaches, such as microwave-assisted solvothermal methods that can offer controlled nanomorphologies, advanced chemical and structural characterizations, and electrochemical evaluation with Li and carbon anodes are being pursued. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships will be developed.

STATUS OCT 1, 2010: Developed (i) stabilized 4 and 5 V spinel cathode compositions through self-surface segregation and chemical-surface modifications, (ii) microwave-assisted solvothermal and template-assisted syntheses of cathodes based on polyanions with nanorod and nanowire morphologies, and (iii) an understanding of their structure-composition-property-performance relationships.

STATUS SEP. 30, 2011: Development of (i) an understanding of the self-surface segregation of cations during the synthesis process of high-voltage (4.7 V) spinel oxide cathodes through advanced characterization methodologies, (ii) novel solution-based synthesis approaches to obtain high-capacity nanostructured polyanion (silicate and phosphate) cathodes, and (iii) an understanding of their structure-composition-property-performance relationships.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, 10-year life, <20% capacity fade over a 10-year period

MILESTONES:

- (a) Understand self-surface segregation of cations in high-voltage spinel cathodes. (Mar. 11) **Complete**
- (b) Develop novel synthesis approaches for high-capacity nanostructured silicate and phosphate cathodes. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

LiVOPO_4 crystallizes in three polymorphic modifications (orthorhombic, triclinic, and tetragonal) with a theoretical capacity of 159 mAh/g and an operating voltage of 3.7-4.0 V (depending on the polymorph), leading to higher energy density than that of LiFePO_4 . These polymorphs can be synthesized by various methods including sol-gel, hydrothermal, solvothermal, carbothermal reduction, and chemical lithiation of VOPO_4 . As part of our ongoing activities in exploiting the microwave-assisted synthesis processes as they offer reaction products within a short reaction time with unique nanomorphologies, this quarter the microwave-assisted solvothermal (MW-ST) synthesis of LiVOPO_4 was pursued. All three polymorphs of LiVOPO_4 were obtained within 30 minutes at $< 230^\circ\text{C}$ by conducting the MW-ST process in a novel mixed solvent (ethanol and water) medium. By varying the Li:V:P and the water:ethanol ratios through a total of about 80 reactions, the conditions to obtain nearly phase-pure products of the three polymorphs were identified, as shown in Table 1 below.

Table 1. Major polymorphic modifications of LiVOPO_4 formed under various reaction conditions

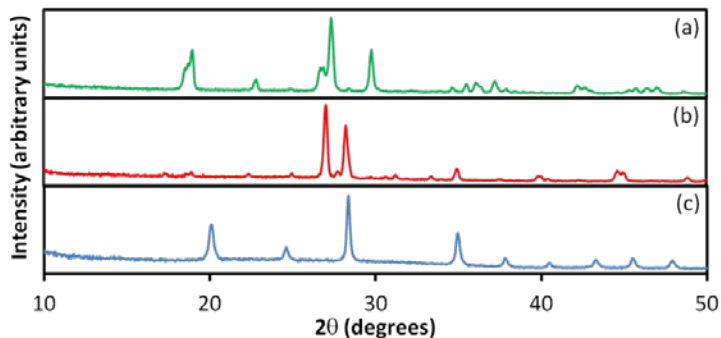
Polymorph	Li:V:P ratio in the reaction mixture	Water:ethanol ratio
Tetragonal	1:1:1	1:3
Tetragonal	2:1:1, 4:1:2	1:1
Tetragonal	3:1:3, 4:1:4, 5:1:5	3:1
Orthorhombic	1:1:3, 1:1:4, 4:1:3	1:3
Orthorhombic	3:1:3	1:0
Triclinic	1:1:3, 2:1:2, 3:1:3, 4:1:4, 5:1:5, 4:1:3, 3:1:2	1:1

The XRD patterns shown in Fig. 1 reveal that highly crystalline phases of the three polymorphic modifications can be obtained by the MW-ST process. ICP analysis indicates slight deviations from the nominal contents due to the presence of trace amounts of impurity phases. Further fine tuning of the conditions to eliminate the minor impurity phases and characterization of the samples by electron microscopy and electrochemical measurements are currently in progress.

Our focus has also been on the synthesis of silicate cathode materials this quarter. It was shown previously that $\text{Li}_2\text{FeSiO}_4$ and $\text{Li}_2\text{MnSiO}_4$ can be synthesized by the MW-ST process in tetraethylene glycol with subsequent furnace heating. Now $\text{Li}_2\text{FeSiO}_4$ has been synthesized by a hydrothermal approach in a mixture of water and ethylene glycol with subsequent heating in a reducing atmosphere. This approach is being extended to obtain $\text{Li}_2\text{Fe}_{1-x}\text{Mn}_x\text{SiO}_4$ solid solutions.

In parallel, our focus has also been on understanding the factors controlling the electrochemical properties of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel, through cationic substitutions and morphological control. Cationic substitutions in $\text{LiMn}_{1.5}\text{Ni}_{0.5-y}\text{M}_y\text{O}_4$ ($\text{M} = \text{Al}, \text{Cr}, \text{Fe}, \text{Co}, \text{Zn}, \text{and Ga}$) eliminate the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ impurity phase, increase the Mn^{3+} content, and suppress the ordering between Mn^{4+} and Ni^{2+} , resulting in an improvement in electrochemical performance. More importantly, segregation of certain $\text{M} = \text{Cr}, \text{Fe}, \text{and Ga}$ ions to the surface during the synthesis process leads to excellent cyclability at 55°C due to a better electrode-electrolyte interface. Furthermore, the variations in the electrochemical properties of undoped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ synthesized by various methods appear to be related to differences in the Mn^{3+} content.

Figure 1. XRD patterns of (a) triclinic, (b) orthorhombic, and (c) tetragonal LiVOPO_4 .



TASK 4.5 - PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE - PROJECT: Cathodes – Development of High Energy Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, cost, cycle life

OBJECTIVES: To develop high-energy, low-cost, and long-life cathode materials.

GENERAL APPROACH: Our approach is to develop high-energy cathode materials using a nano-engineered synthesis process in combination with the surface treatment and optimization of electrolytes/additives. High-voltage LiNi_{0.5}Mn_{1.5}O₄ cathode with surface coating will be investigated using a high-voltage electrolyte. The thermal stability of LiMn_{1-x}Fe_xPO₄ will be investigated to validate its feasibility for PHEV applications. Alternative cathodes, such as high rate (up to 30C) Li₃V₂(PO₄)₃/C and renewable organic cathodes that exhibit two or more electrons per redox center, will also be evaluated as PHEV/EV compatible cathode materials.

STATUS Oct. 1, 2010: Nanoplates of LiMnPO₄ were prepared by a single-step, solid-state reaction with molten hydrocarbon and exhibit a reversible capacity of ~168 mAh/g. A novel cathode material, Li₂CoPO₄F, was synthesized and characterized. Up to 1 mole of Li⁺ ions is reversible in Li₂CoPO₄F within 2.0 to 5.5 V. Organic cathodes allowing multiple electron transportation per redox center were prepared with a reversible capacity of more than 200mAh/g. High-voltage LiNi_{0.5}Mn_{1.5}O₄ with a reversible capacity ~130 mAh/g was successfully synthesized with a cost-effective approach suitable for mass production.

STATUS SEP. 30, 2011: The thermal stability of iron-doped LiMnPO₄ will be evaluated. The investigation of the electrochemical performance of non-stoichiometric LiMnPO₄ will be completed. The coulombic efficiency and cycle life of high-voltage LiNi_{0.5}Mn_{1.5}O₄ will be improved by using high-voltage electrolytes/additives and appropriate surface coatings. The performance of a high-rate Li₃V₂(PO₄)₃/carbon composite will be investigated. Anthraquinone-based polymer cathode materials will be synthesized, and their operational voltage of this high-capacity material will be tuned by adjusting the functional groups to further improve its energy density.

RELEVANT USABC GOALS: >96 Wh/kg (PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:

- (a) Evaluate thermal stability of iron-doped LiMnPO₄. (Mar. 11) **Complete**
- (b) Synthesize and characterize the high-rate Li₃V₂(PO₄)₃/carbon composite. (Jun. 11) **Complete**
- (c) Identify the compatible electrolyte/additive and develop an appropriate surface-coating for the high-voltage cathode, LiNi_{0.5}Mn_{1.5}O₄. (Sep. 11) **Delayed, due Dec. 11**
- (d) Synthesize and characterize high-capacity organic cathodes based on the quinonyl group. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Most milestones for FY11 have been accomplished. The thermal stability of electrochemically delithiated LiMnPO_4 cathode was investigated. The results from the hot-plate x-ray and TGA-DSC-MS show that the weight loss observed in TGA curves between room temperature and *ca.* 470°C is associated with the amorphization of MnPO_4 . Oxygen release and associated structure change occurred at a temperature of more than 490°C. Several vanadium-based cathodes have been developed. The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ /carbon composite showed an excellent high rate capability and LiV_3O_8 nanorods exhibited a capacity of more than 250 mAh/g at 100 cycles. Cr-doping in high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ increased the content of the disordered phase in the spinel and significantly improved the cycling stability of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$.

The effects of electrolyte additive and coin cell cans have been investigated during the last quarter. Figure 1 shows that a low concentration of LiBOB additive (0.25 to 0.5%) in 1M LiPF_6 in EC-DMC largely improved the cycling stability of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$ cathode, especially at high discharge rate. This improvement can be attributed to the formation of a stable SEI layer on the cathode when a low concentration of LiBOB was added to the electrolyte. Fig. 2 shows the cyclic voltammetry curves of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$ in a stainless steel can (MTI Inc.). A sharp current peak associated with the oxidation of the S.S. can was observed when voltage was increase to more than 4.8 V during the first anodic scan. The initial coulombic efficiency of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$ was increased from 77.7 to 87.3% after employing Al-clad cathode cans.

In addition, a new organic cathode material, poly(1,8-anthraquinonyl sulfide) (P18AQS), was synthesized. The capacity and power rate of P18AQS based cathode (see Fig. 3) were smaller than those of poly(1,5-anthraquinonyl sulfide) (P15AQS), which has a sulfur substitution position with less steric-stress. These results have shined light on the rational design of new quinone-based organic cathodes.

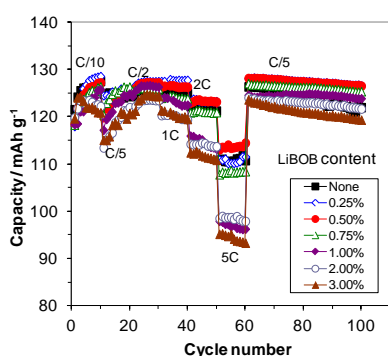


Figure 1. Low concentration (0.25-0.5%) LiBOB additive can significantly improve the first cycle efficiency and rate capability.

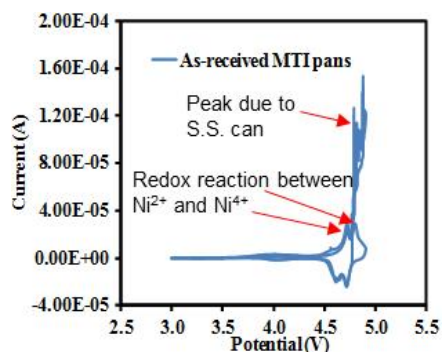


Figure 2. The cyclic voltammetry curves of $\text{LiNi}_{0.45}\text{Cr}_{0.05}\text{Mn}_{1.5}\text{O}_4$ in a stainless steel can.

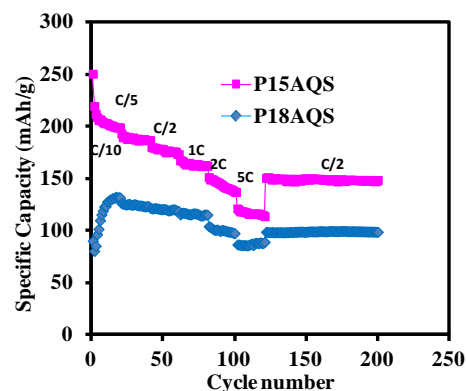


Figure 3. Comparison of the rate capabilities of novel organic cathodes with more than one redox center.

Collaborations: Dr. Xu, ARL (new electrolyte); Prof. Whittingham, Binghamton U. (magnetic measurements of spinels).

Publications:

1. J. Xiao, N.A. Chernova, S. Upreti, X. Chen, Z. Li, Z. Deng, D. Choi, W. Xu, Z. Nie, G.L. Graff, J. Liu, M.S. Whittingham and J.-G. Zhang, "Electrochemical Performances of LiMnPO_4 Synthesized from Non-Stoichiometric Li/Mn Ratio," *Phys. Chem. Chem. Phys.* DOI: 10.1039/c1cp22658d.
2. D. Choi, J. Xiao, Y.J. Choi, J. S. Hardy, M. Vijayakumar, M.S. Bhuvaneshwari, J. Liu, W. Xu, W. Wang, Z. Yang, G. Graff and J.-G. Zhang, "Thermal Stability of Electrochemically Charged/Discharged LiMnPO_4 Nanoplate Cathode for Li-ion Battery," *Energy. Environ. Sci.* DOI: 10.1039/c1ee01501j.
3. J. Yu, K.M. Rosso, J.-G. Zhang and J. Liu, "Ab initio study of lithium transition metal fluorophosphate cathodes for rechargeable batteries," *J. Mater. Chem.*, **21**, 12054 (2011).

TASK 4.6 - PI, INSTITUTION: John B. Goodenough, The University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – Liquid Cathode Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Stable solid electrolyte with $\sigma_{\text{Li}} > 10^{-4}$ S/cm

OBJECTIVE: To explore use of an existing solid Li⁺-ion electrolyte with $\sigma_{\text{Li}} > 10^{-4}$ S/cm that, though unstable in contact with an acidic aqueous cathode solution, may be stable in a non-acidic solution or if coated with a protective layer. By stabilizing the electrolyte against degradation, which we have shown to be due to the presence of Ti(IV) in the available electrolyte, we can obtain data on the specific capacity versus molar fraction of the Fe³⁺/Fe²⁺ couple in the cathode solution and how capacity is retained at higher discharge/charge rates. We can obtain data on the ability of seals to prevent water crossover into the anode compartment and on different cathode current-collector configurations. We will also explore composite polymer/inorganic Li⁺-ion solid electrolytes in order to develop thin, tough, flexible membranes in collaboration with a polymer chemist. This approach to an alternative cathode can be realized with either a Li⁺-ion or a Na⁺-ion solid electrolyte, and a search for an alternative solid electrolyte will be made.

GENERAL APPROACH: Exploration of limitations of an aqueous Fe(II)/Fe(III) cathode and of Li⁺ and Na⁺ solid electrolytes.

STATUS OCT. 1, 2010: A test cell and seals were constructed with the existing commercially-available Li⁺-ion electrolyte Li_{1.3}Ti_{1.7}Al_{0.3}(PO₄)₃. The stability of the electrolyte versus a non-acid aqueous solution for the Fe³⁺/Fe²⁺ couple was tested.

STATUS SEP. 30, 2011: The concept of a liquid-cathode battery with the existing commercial solid electrolyte will have explored more fully. A possible polymer/inorganic-solid composite will be examined as a viable thin, tough, flexible solid-electrolyte membrane. Investigations will be initiated on alternative materials for the Li⁺-ion or Na⁺-ion solid electrolytes.

RELEVANT USABC GOALS: Available specific energy density > 80 Wh/kg, 5000 deep-discharge cycles, 15-year calendar life.

MILESTONES:

- (a) Test liquid-cathode Li battery in which the pH of the cathode solution is alkaline. (Feb. 11) **Complete**
- (b) Test a composite Li⁺-ion solid electrolyte. (Feb. 11) **Complete**
- (c) Test feasibility of coating the existing solid electrolyte with a protective coat against reduction by an acidic solution. (May 11) **Preliminary complete**
- (d) Identify a new Li⁺-ion or Na⁺-ion solid electrolyte. (Sep. 11) **Initiated, due Sep. 12**

PROGRESS TOWARD MILESTONES

Realization of a competitive rechargeable battery to power electric vehicles requires a fast charge rate and increased energy density at lower cost. The driving range at a given power output $P=IV$ depends on the energy stored reversibly $\int_0^{\Delta t} IV(t)dt = \int_0^Q V(q)dq$ per unit weight/volume delivered in a time Δt at a current $I=dq/dt$. The charge Q transferred between electrodes in a time Δt is the capacity. With present strategies for Li-ion batteries, the capacity of a cell is limited by the reversible solid-solution range of Li in the host cathode and the voltage is limited by the window of the liquid electrolyte. The development of a solid Li^+ electrolyte stable on contact with a Li anode and an oxide valence band would allow development of rechargeable batteries not only with a Li anode capable of a fast charge, but also with a cathode consisting of high-voltage insertion compounds or alternative cathode strategies. Therefore, our effort this year has focused on the realization of an oxide Li^+ electrolyte $\sigma_{\text{Li}} > 10^{-4} \text{ S cm}^{-1}$ that is stable on contact with a Li anode.

We have concentrated on oxides with the garnet framework, which has an interstitial space consisting of tetrahedral sites $24d$ bridged by octahedral sites $48g$ sharing a common face as illustrated in the Fig.1 for a maximum 7.5 Li^+ per formula unit. Last quarter, we reported our preparation and characterization of nominal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; from those data we concluded that the optimum Li^+ conductivity should be in the range 6.2 to 6.6 Li^+ per formula unit. The $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is only stable above 800°C if the sample absorbs adventitious Al^{3+} taken up from the alumina crucible in which it was fired. This quarter we used neutron diffraction to show that Al^{3+} is located in the interstitial $48g$ octahedral site with empty tetrahedral $24d$ sites on either side. We have also obtained a $\sigma_{\text{Li}} \approx 10^{-3} \text{ S cm}^{-1}$ by substituting Ta for Zr, Fig.2. We investigated composite electrolytes consisting of the garnet and a sintering aid such as an $\text{Al}_2\text{O}_3/\text{SiO}_2$ mix. We found, for example, that the grain boundaries of these composites are attacked in a $\text{pH} < 12$. We have begun to investigate silicates for alternative Li^+ or Na^+ electrolytes. We also stabilized the $R\bar{3}c$ NASICON structure for $\text{LiZr}_2(\text{PO}_4)_3$ with Ca substitution.

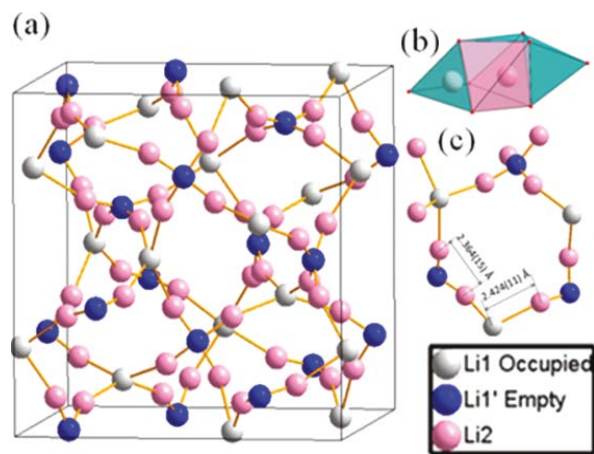


Figure 1. Li^+ positions in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.

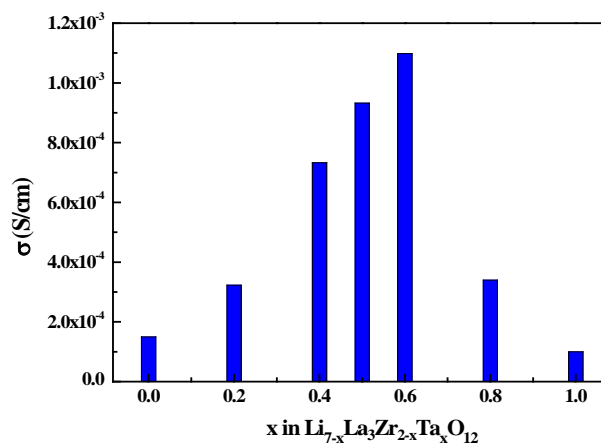


Figure 2. Relationship of conductivity and x in $\text{Li}_{7-x}\text{La}_3\text{Zr}_2\text{O}_{12}$.

TASK 4.7 - PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes – Positive and Negative Electrodes: Novel and Optimized Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-energy-density, poor cycle life, safety.

OBJECTIVES: Understand the relationship between particle size-shape and electrode performance. Understand the structure-composition-properties relationship for high voltage spinel electrodes. Understand the chemical and physical phenomena behind the reactivity of negative electrode materials based on metal oxides. Design materials that yield high capacities upon extended cycling.

GENERAL APPROACH: Employ synthesis methods that lead to well controlled particle sizes and shapes, and explore the effect of reaction conditions on the final composition and microstructure. Evaluate changes in properties and morphology upon cycling, and correlate them with the micro and crystal structural features. Use several characterization techniques (diffraction, spectroscopy, microscopy, electroanalysis) to get a complete picture of the different reactions involved in lithium-ion battery electrodes (intercalation, conversion, alloying). .

STATUS OCT. 1, 2010: The performance of LiNi_{1/2}Mn_{3/2}O₄ made using solvothermal routes was evaluated. Nanometric Sn particles showing narrow size and shape distributions were prepared and tested. The conversion reaction of NiO was studied by Li NMR, O K edge XANES and TEM. The search for novel Cu-M-O phases has not led to satisfactory results and, at this point, has been discontinued.

STATUS SEP. 30, 2011: The effect of particle size on the thermal behavior of cycled LiNi_{1/2}Mn_{3/2}O₄ electrodes will have been evaluated. The effect of different annealing treatments on the structure, composition, and performance of LiNi_{1/2}Mn_{3/2}O₄ will have been analyzed. The electrochemical response of NiO during conversion will have been studied at different temperatures. The changes in size and morphology with cycling will have been studied for Sn nanoparticles. Efforts will be directed at making electrodes with these nanoparticles.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles.

MILESTONES:

- (a) Report the thermal analysis of cycled LiNi_{1/2}Mn_{3/2}O₄ electrodes and the results of annealing using different treatments. (Mar. 11) **Complete**
- (b) Report the analysis of Sn nanoparticles at different stages of cycling. (Sep. 11) **Partially complete; change in research direction.**
- (c) Report the electrochemical response of NiO when cycled at high temperatures. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Collaborations: Prof. Grey (SUNY Stony Brook), Drs. Persson, Battaglia, Dong, Doeff, Richardson, Chen, Guo, Yang, Kostecki (LBNL), Dr. Casas-Cabanas (CRISMAT, France), Dr. Palacin (ICMAB, Spain).

The analysis of the electrochemical conversion of NiO in a Li battery at different temperatures was completed during this quarter. This system was taken as model to understand the fundamentals of conversion reactions and the underpinnings of their inefficiencies. Figure 1 (top) shows the first cycle of two different batteries cycled at: i) room temperature using 1 M LiPF₆ in EC:DMC 1:1 as electrolyte, ii) 100°C using 1 M LiTFSI in EC. Both cells were cycled at C/4. A significant upward shift of the plateau of conversion, from *ca.* 0.7 to 0.95 V, was observed when the temperature was raised, thereby reducing the voltage hysteresis. This observation indicates that a significant portion of this hysteresis, which is ubiquitous in compounds following this reactivity, has a kinetic component, with the thermodynamic potential being far from that observed at room temperature. The cells were also allowed to relax at OCP at different points of the reaction. Representative examples after cutting off at 0 V, are shown in Fig. 1 (bottom). In general, relaxation of the potential value was not observed even after as many as 500 h. The shapes of the relaxation curve departed from the asymptotic behavior observed in conventional intercalation electrodes, suggesting that side reactions may be occurring even in open circuit. The existence of these side reactions adds another complication that seriously questions the viability of these reactions for application, in this case, in terms of shelf life. The voltage difference between the closed circuit and that read at the end of the relaxation (150 h in Fig. 1) was systematically larger for the experiment at room temperature.

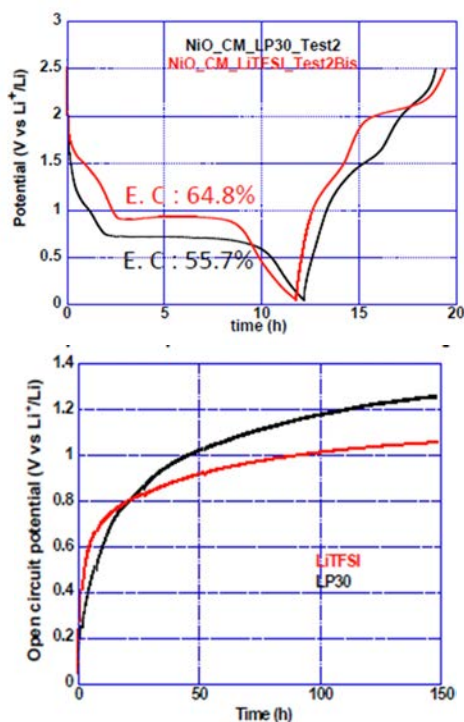


Figure 1: (Top) Profile of the first cycle of a NiO electrode at room temperature (black) and at 100°C (red); (Bottom) evolution of the open circuit potential after the 1st discharge.

The status as of September 30th differed slightly from what was initially planned due to changes in program priorities. All tasks related to milestone (c) were complete, as indicated above. Work toward milestone (b) was redirected after obtaining Sn particles with unprecedentedly clean surfaces in order to analyze the effect of controlled surface oxidation in air (see Q3 report). The tasks under milestone (a) were redirected to focus on the crystal-chemistry of LiNi_{1/2}Mn_{3/2}O₄, within one of the sub-tasks in the *NiMn Spinel Focus Group*. A thorough study of the effect of annealing on the ordering, composition, and electrochemistry of this material, which combines tools such as NMR, magnetic susceptibility, and diffraction, was conducted (see Q3 report). In addition, spectroscopic analysis of the electronic structure upon Li removal, not initially planned in the AOP, was performed. Publication of the results is expected in FY12.

Publication this quarter:

“Comparison of the Performance of LiNi_{1/2}Mn_{3/2}O₄ with Different Microstructures”, J. Cabana, H. Zheng, A.K. Shukla, C. Kim, V.S. Battaglia, and M. Kunduraci, *J. Electrochem. Soc.* **158**, A997 (2011).

BATT TASK 5 DIAGNOSTICS

TASK 5.1 - PI, INSTITUTION: Robert Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial Processes: Diagnostics

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: Low energy (related to cost), poor Li battery calendar/cycle lifetimes.

OBJECTIVES: (i) Establish direct correlations between electrochemical performance of high-energy Li-ion composite cathodes, and surface chemistry, morphology, topology and interfacial phenomena, (ii) improve the capacity and cycle-life limitations of Li-alloy anodes.

GENERAL APPROACH: Our approach is to (i) apply *in situ* and *ex situ* Raman and FTIR far field and near field spectroscopy/microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, electron microscopy (SEM, HRTEM), and standard electrochemical techniques to detect and characterize bulk and surface processes in intermetallic anodes, and high-energy cathodes, (ii) design and apply a new model electrochemical experimental setup to study the kinetics of lithium alloying and diffusion in intermetallic anodes, and possible correlations with the formation and long-term stability of the SEI layer,

STATUS OCT. 1, 2010: Defined the physico-chemical parameters of the intermetallic alloys and their interfacial properties that determine long-term electrochemical performance of intermetallic anodes in Li-ion systems. These include: (i) charge and mass transfer parameters for Sn, Si, and Al alloys, (ii) basic electrocatalytic properties of alloy materials, (iii) the effect of material structure, crystallinity, morphology and composition. *In situ* and *ex situ* Raman and FTIR spectroscopy were used to determine and characterize surface and bulk processes in composite LiMnPO₄ cathodes.

STATUS SEPT. 30, 2011: To gain insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes and evaluate their impact on the electrode long-term electrochemical behavior. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. *In situ* and *ex situ* far- and near-field FTIR and Raman spectroscopy will be employed in conjunction with AFM surface imaging, which will be applied to detect and monitor surface phenomena at the intermetallic anodes. Similar experimental methodology will be used to detect and characterize surface and bulk processes in high-energy layered NMC and Ni-Mn spinel cathodes.

RELEVANT USABC GOALS: *Cycle life:* 5000 (deep) and 300,000 (shallow) cycles. *Available energy:* 96 Wh/kg. *Calendar life:* 15 years.

MILESTONES:

- (a) Identify the structural and surface changes of Si and Sn model anodes working collaboratively with the BATT Anode Group. (Jul. 11) **Complete**
- (b) Carry out preliminary near-filed measurements of SEI layers on Si, Sn anodes and high voltage cathodes. (Sep. 11) **Complete**
- (c) Characterize surface phenomena in high-voltage composite cathodes. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

The focus of our work in the 4th quarter of FY11 included *in situ* spectro-electrochemical studies of the high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel (LMNO) cathode. *In situ* Raman spectra that were collected from a model electrode composed of LMNO powder pressed onto Al foil (binder and carbon-free) were obscured by a strong fluorescence signal. Moreover, the intensity of fluorescent background grew higher during prolonged electrode polarization/cycling measurements. Fluorescence, which originates from electrolyte decomposition products that form as a result of electrochemical and chemical side reactions, is an undesirable effect that interferes with observation of Raman features from the electrode. This time it was decided to take advantage of this phenomenon by using *in situ* fluorescence spectroscopy of model LMNO electrodes to provide a real-time probe of the formation of a surface electrolyte interphase (SEI) on the particle during cycling of the electrode.

The fluorescence intensity of a single LMNO particle was measured *in situ* as it was potentiostatically cycled three times between 3.5 and 5.0 V with 1 M LiPF_6 in EC:DEC (1:2 w/w) electrolyte (Fig. 1). The electrochemical data, plotted as current vs. time, show two active regions with good reversibility. A slight excess of Mn^{3+} present in the pristine powder is responsible for the first small peak at 4.05 V. The two sharp peaks at 4.71 and 4.77 V are attributed to the $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ redox reactions, respectively. During the first potential sweep to 5.0 V, a sharp rise in fluorescence intensity occurred at the beginning of the Ni^{2+} oxidation reaction near 4.7 V that continued until the reverse scan caused Ni^{4+} reduction at the beginning of the relithiation process. Interestingly, the fluorescence signal declined after this point until Ni^{2+} oxidation during the potential sweep on the second cycle occurred again. This pattern, repeated for all three cycles, strongly suggests that electrolyte decomposition is catalyzed by the changes that occur upon Ni oxidation during the delithiation process. In addition, the loss of fluorescence intensity indicates that most of these fluorescent decomposition products either dissolve into the electrolyte, or decompose to other products right after formation. However, the rising d-fluorescence background intensity in Fig. 1 demonstrates that some fluorescent species remained at the particle surface. A similar increase in fluorescence has also been observed from 1 M LiClO_4 in EC:DEC electrolyte solutions. Therefore, the fluorescent species likely originate primarily from decomposition of the carbonate-based electrolytes, as opposed to LiPF_6 . These results complete milestone (c).

Single crystal studies of Sn have demonstrated that different crystal facets have different mechanisms of SEI layer formation (milestone “a”). Future Si single crystal studies are planned. Preliminary near-field measurements on HOPG model electrodes, Sn anodes, and Li_xFePO_4 single particles were carried out using the near-field spectroscopy instrumentation at JASCO and Nea. A

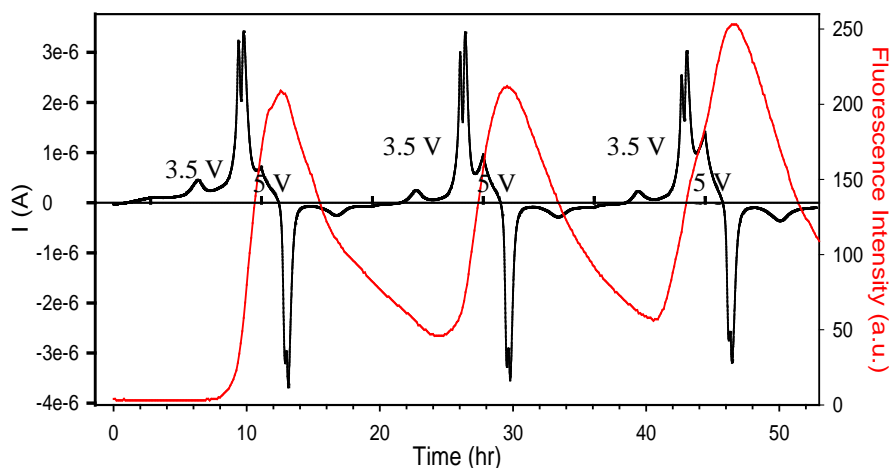


Figure 1. Current (left axis) and fluorescence intensity (right axis) vs. time during three potential sweeps between 3.5 and 5.0 V at 0.05 mV/s.

similar instrument setup from Neaspec will be purchased in October with capital equipment funding recently received that will enable future in-house spectroscopic measurements at the nanoscale (nanoRaman, *i.e.*, TERS and nano-FTIR) to characterize cathode and anode interfacial structures.

TASK 5.2 - PI, INSTITUTION: Xiao-Qing Yang, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics – Battery Materials: Structure and Characterization

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: PHEV: energy density, cycle life; HEV: power density, abuse tolerance.

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density lithium battery with better safety characteristics and longer life. The second objective is to design, synthesize and characterize new electrolytes for PHEV oriented high energy density Li/air batteries. Special attention will be given to the new non-aqueous electrolytes with the capability to dissolve Li₂O and Li₂O₂ oxides for Li/air batteries. Testing facilities for high energy Li/air cells and the testing cells using these new non-aqueous electrolytes, as well as gas diffusion electrodes for Li/air cell, will be constructed and investigated at UMASS Boston.

GENERAL APPROACH: Our approach is to use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish the structural differences between surface and bulk of electrodes. Time resolved X-ray diffraction (TRXRD) technique will be used to understand the reactions that occur in charged cathodes at elevated temperatures. *In situ* XRD with PSD detector will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at various C rates. These approaches developed at BNL will be available to other BATT members through extended collaboration. For the task of high energy lithium-air cells, our approach is to combine the organic synthesis and in situ characterization capability with the expertise of air-metal batteries at UMASS Boston to reach the proposed objectives.

STATUS OCT. 1, 2010: We have completed the studies on the structural characteristics of different types of LiFe_{1-x}M_xPO₄ (M=Mn, Co, and Ni) phosphate cathode materials using various synchrotron X-ray techniques. The studies of LiFe_{1-x}Mn_xPO₄ (x=0.2, 0.4, 0.6, and 0.8) have been completed using *in situ* XRD and XAS spectroscopies.

STATUS SEP. 30, 2011: We will continue our studies on the structural characteristics of different types of lithium iron phosphate cathode materials with mesoporous structure, as well as layer structured Li_{1.2}Mn_{0.6}Ni_{0.2}O₂ cathode materials (in collaboration with ANL) using various synchrotron X-ray techniques. We will continue our Li/air battery studies in non-aqueous electrolytes with gas diffusion electrodes made of carbon materials with various morphologies.

RELEVANT USABC GOALS: 15 year life, <20% capacity fade over a 10-yr. period.

MILESTONES:

- (a) Complete soft XAS studies of Li_{1.2}Mn_{0.6}Ni_{0.2}O₂ cathode materials during electrochemical cycling. (Apr. 11) **Complete**
- (b) Complete the studies of carbon structure effects on the electro-catalysis performance of air cathode in Li/air cells. (Apr. 11) **Complete**
- (c) Complete *in situ* x-ray diffraction studies of lithium iron phosphate cathode materials with mesoporous structure in comparison with large particle sized cathode during electrochemical cycling. (Sep. 11) **Complete**
- (d) Complete the studies of increasing the solubility of oxygen in Li/air electrolytes. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

In the 4th quarter of FY 2011, progress toward milestones has been made. All of the milestones for FY2011 have been successfully completed.

During the 4th quarter of FY2011, research at BNL was focused on the comparative study of the structural changes of $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ cathode material between samples with and without a mesoporous structure during electrochemical charge-discharge cycling. In collaboration with Prof. Hong Li and his research group at the Institute of Physics, Chinese Academy of Sciences, *in situ* and *ex situ* XRD studies were carried out. Milestone (c) was completed. The phase transformation behaviour is quite different for samples synthesized with and without mesopores. The sample without a mesoporous structure undergoes a conventional two-phase reaction starting at the beginning of the first plateau on the charge curve and showing no delay of the phase transition. At the end of charge at 5 V, the phase transition to the third phase is not completed. In contrast, for the mesoporous sample, new crystallized phases can only be observed at the end of the first plateau on the charge curve. The transition to the third phase was almost completed at the end of charge at 5.0 V. These results show that the phase transition behaviour of $\text{LiMn}_{0.4}\text{Fe}_{0.6}\text{PO}_4$ is closely related to the morphology of the sample.

In collaboration with Prof. Qu and his team at the University of Massachusetts (UMASS) at Boston, milestone (d) for a Li/air battery was completed. Among all of the challenges for developing practical Li/air batteries, increasing the oxygen solubility in non-aqueous electrolytes is quite critical, since the required rate capability of the gas diffusion electrode (GDE) in a Li/air cell will never be met if such solubility cannot be increased to a level close to that found in an aqueous electrolyte. The BNL-UMASS team has developed a new approach to solve this problem: using perfluorotributylamine (FTBA) as an additive for increasing O_2 solubility in the non-aqueous electrolyte of LiPF_6 in propylene carbonate (PC) solvent. Figure 1 shows the comparison of the diffusion-limited current of the O_2 reduction on a powder microelectrode filled with activated carbon. It can be seen that about a 4x increase of the diffusion-limited current for the O_2 reduction is achieved on the carbon electrode in the PC based electrolyte with the addition of FTBA.

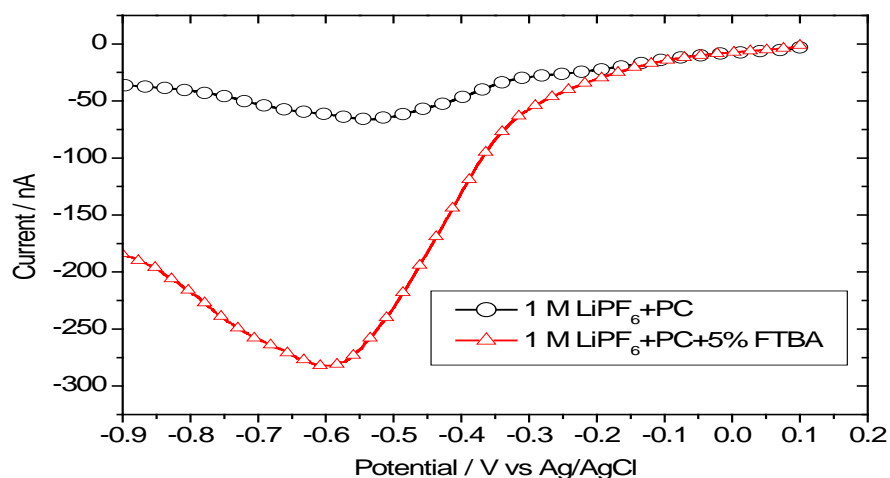


Figure 1. Linear sweep voltammetry of oxygen reduction on a Norit-A carbon microcavity electrode (cavity diameter: 0.05 mm), scan-rate: 1 mV s^{-1}

TASK 5.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, SUNY Stony Brook/Cambridge University

TASK TITLE - PROJECT: Diagnostics – First Principles Calculations and NMR Spectroscopy of Electrode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low rate capabilities; high cost; poor stability; low energy-density

OBJECTIVES: Determine the effect of structure on stability and rate capability of cathodes and anodes. Explore relationship between electrochemistry and particle size and shape. Develop new, stable, cathode materials with high energy-density.

GENERAL APPROACH: Use solid state NMR and diffraction/TEM to characterize local and long-range structure as a function of particle size, sample preparation method, state of charge and number of charge cycles (cathodes). Use electrochemistry to correlate particle size with rate performance. Continue to develop the use of *in situ* NMR methods to identify structural changes and reactivity in oxides and intermetallics and to examine Li dendrite formation. Use first-principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure and particle size on cell voltages and rate capability. Use high-throughput computing to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT 1, 2010: *In situ* NMR and XRD experiments will be ongoing. Several compounds from computational search will continue under experimental investigation.

STATUS SEP. 30, 2011: Go no-go decision will be made on one or two new cathode materials. Initial surface characterizations will be finished. Insights will be gained into the viability of several Na cathodes. Rate performance *vs.* local structure correlations will be established for Li(Ni_{0.5}Mn_{1.5})O₄.

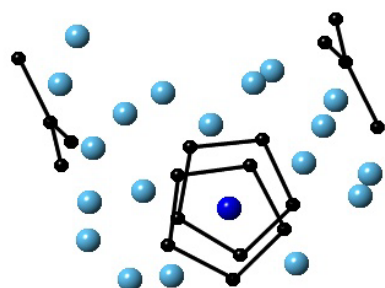
RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:

- (a) Initiate Na calculations. (Mar. 11) **Complete**
- (b) Initiate electrochemical testing of one cathode materials in sidorenkite class. (Mar. 11) **Complete**
- (c) Initiate surface characterization. (Mar. 11) **Complete**
- (d) Investigate two new cathode materials and structurally characterize. (Sep. 11) **Complete**
- (e) Explore Li dendrite formation on a series of ionic liquids. (Sep. 11) **On-going, due Dec. 11**
- (f) Investigate local structure in various Li(Ni_{0.5}Mn_{1.5})O₄ spinels and compare with rate performance. (Sep. 11) **Complete**

PROGRESS TOWARD MILESTONES

Silicon has attracted considerable interest as an anode material for high-energy Li-ion batteries due to its very high specific capacity (3579 mAh/g). Efforts in this reporting period have focused on developing methods to establish how Si's operating behavior is affected by the size and morphology of the Si particles, making use of new experiments involving ^{29}Si NMR spectroscopy. Unfortunately, analysis of the Si substructure by the direct probe ^{29}Si has been hampered by the low signal-to-noise ratio and the difficulty in interpreting the usually very broad and poorly resolved spectra of lithiated Si particles. Thus, we have developed a number of suitable NMR techniques for the determination of both Si-Si and Li-Si connectivities, which make use of covalent interactions between Si atoms (J-coupling) and through-space (dipolar) interactions between nuclei. The



approach is demonstrated with the crystalline lithium silicide $\text{Li}_{12}\text{Si}_7$ (Fig. 1). Its structure includes 5-membered Si rings which are stacked in one-dimensional chains, as well as 4-membered Si "Y" stars located in the planes between the Si_5 rings, as shown in Fig. 1.

Figure 1. Fragment of the crystal structure of $\text{Li}_{12}\text{Si}_7$ showing the Si_4 stars and the Si_5 rings (black) and Li atoms in light/dark blue.

Figure 2 shows a two-dimensional (2D) NMR experiment that investigates covalent interactions (bonds) between atoms (^{29}Si INADEQUATENMR). In this spectrum, two bonded atoms giving rise to resonances with frequencies ν_1 and ν_2 result in a correlation at $\nu_1 + \nu_2$ in the indirect dimension of the 2D spectrum. No correlations are seen for non-bonded atoms. Consistent with this, separate sets of connectivities are seen between the Si atoms in the rings (resonances b, c, d, e, and g) and the stars (a, f, h and i).

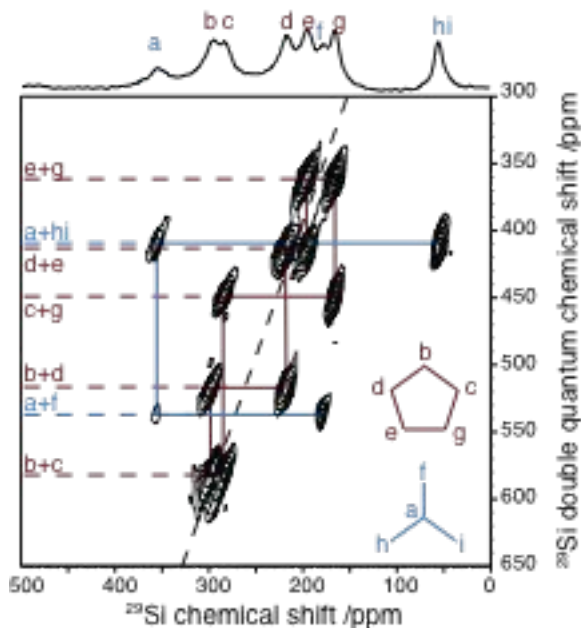


Figure 2. Experimental one-pulse spectrum (top) and ^{29}Si 2D INADEQUATE NMR spectrum of $\text{Li}_{12}\text{Si}_7$ at 233 K. The dashed line represents the $2\nu-\nu$ line. Solid lines are added so as to follow the Si-Si connectivities.

These experiments, along with NMR experiments designed to measure Li-Si connectivities are being employed to investigate structure in cycled ^{29}Si -enriched battery materials. In parallel to this method development, we have now (i) established a method to perform *in situ* NMR experiments of carboxymethyl-cellulose coated Si nanoparticles, so that we can now study this chemistry *in situ*, and (ii) performed detailed *ex situ* NMR studies of Si nanoparticles. The data for Milestone (c) has been collected and its analysis is ongoing. The project will be completed by the end of 2011.

Task 5.4 - PI, INSTITUTION: Yang Shao-Horn, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Diagnostics – Studies and Design of Chemically and Structurally Stable Surfaces and Structures of Lithium Storage Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: High cost, poor cycle and calendar life and abuse tolerance of Li-ion batteries

OBJECTIVES: To develop high-energy and long-cycle-life cathodes.

GENERAL APPROACH: The surface-chemistry, microstructure of oxide-electrolyte interface with and without surface modification, and oxide crystal structure will be examined by scanning TEM, synchrotron XRD and XAS, and XPS. These surface and structural features and their changes during electrochemical measurements would provide insights into the nature of interfacial stability between oxide and electrolyte and developing strategies in the design of stable interfaces for high-energy and long-cycle-life cathodes.

STATUS OCT. 1, 2010: The surface-chemistry comparison of pristine and cycled LiNi_{0.5}Mn_{0.5}O₂ and LiCoO₂ as a function of depth from surface using angle-resolved XPS was completed; from this a working hypothesis on surface species stabilizing the cathode surface was proposed.

STATUS SEP. 30, 2011: Changes in the surface chemistry of select Li-rich (Li₂O)_x.(MO₂)_y (where M = Mn, Co, Ni, etc.) layered compounds will be identified and compared with those of LiNi_{0.5}Mn_{0.5}O₂ and AlPO₄-coated LiCoO₂. Application of fundamental insights to design of new and stable surfaces for high-energy cathodes will be ongoing.

RELEVANT USABC GOALS: High energy/power ratio battery, energy density (>100 Wh/kg, power density (>400 W/kg), 15-year calendar life and cycle life (5,000 cycles).

MILESTONES:

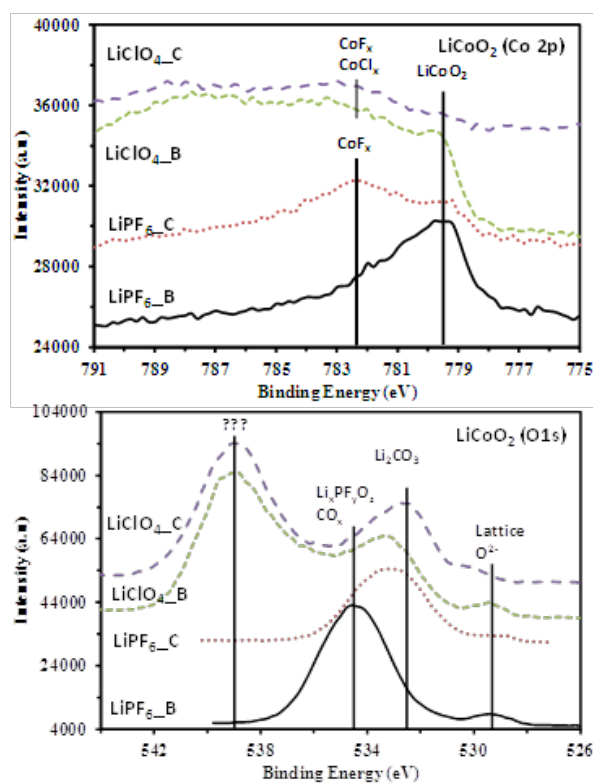
(a) Survey, synthesize, and test select Li-rich (Li₂O)_x.(MO₂)_y (where M = Mn, Co, Ni, etc.) layered compounds. (Mar. 11) **Complete**

(b) Collect and analyze XPS and TEM data to study the surface-chemistry changes of select Li-rich (Li₂O)_x.(MO₂)_y during charge and discharge. (Sep. 11) **On-going, due Dec. 11**

PROGRESS TOWARD MILESTONES

The objective of this project is to develop the fundamental understanding necessary to design stable surfaces and structures for Li storage. In an effort to increase the depth of the region analyzed by XPS, we have taken advantage of synchrotron radiation on beamline X24A at NSLS and collected the spectra utilizing monochromatic X-rays with energy of 2555 eV compared to conventional Al K_{α} X-rays with energy of 1487 eV.

In this way, the depth of the analyzed region increased from *ca.* 4 to 11 nm for photoelectrons associated with the Co 2p region. We investigated the surface chemistry of bare and “AlPO₄”-coated LiCoO₂ cathodes after 20 cycles at C/5 in 1M LiPF₆ and LiClO₄ in a 3:7 volume ratio of EC:DMC between voltage limits of 2.0 to 4.6 V *vs.* Li with a 4 hr hold at 4.6 V. The coated LiCoO₂ electrode cycled in LiPF₆ has higher capacity retention than the bare electrode cycled in LiPF₆ or bare and coated electrodes cycled in LiClO₄. It is interesting to note that the bare electrode cycled in LiClO₄ has higher capacity retention than the bare electrode cycled in LiPF₆ or the coated



electrode cycled in LiClO₄. Hence, the coating does not provide an advantage when cycling was performed in LiClO₄ electrolyte. The Co 2p synchrotron-based data (top curves) for the bare LiCoO₂ electrode are consistent with conventional data showing mostly a contribution from LiCoO₂. However, the Co 2p spectra for the coated-LiCoO₂ electrode cycled in LiPF₆ display a contribution from LiCoO₂ in addition to the CoF_x contribution, which is the only spectra observed in the case of the conventional data. Therefore, the depth of the region that contains CoF_x for the coated electrode cycled in LiPF₆ is greater than 4 but less than 11 nm. The formation of CoF_x appears to also occur in the case of the electrodes cycled in LiClO₄ as the surface doesn't contain enough chlorine to account for all of the highly oxidized Co. The extent of the formation of CoF_x is greater in the case of the coated electrode relative to the bare electrode which has the lowest degree of capacity retention among all electrodes. Such high binding energy of the Co peak was also observed in conventional data and cannot be attributed to differential charging. In this

case, the formation of CoF_x suggests an interaction with the PVDF binder since it is the only source of F. Such an interaction could lead to degradation of PVDF and the loss of electrical connectivity between particles, and be responsible for the poor performance. The O 1s photoemission spectra (bottom curves) are qualitatively similar to conventional spectra with one very noticeable exception. The electrodes cycled in LiClO₄ but not those cycled in LiPF₆ have a large peak at high binding energy due to differential charging and, therefore, suggests that the species formed on the surface of the LiClO₄ cycled electrodes are more resistive in nature than those formed as a result of cycling in LiPF₆. High binding energy peaks due to sample charging were also observed in the F 1s as well as the Al 2p and Al 2s spectra and were all shifted by similar amounts. Sample charging occurs more frequently when monochromatic X-rays rather than conventional X-rays are used.

Collaborations: Continued with Dr. A.N. Mansour at the NSWC in XPS and XAS measurements through a subcontract of MIT. Continued with M.M. Thackeray in using TEM to study the atomic structure of Li_xNi_{0.25}Mn_{0.75}O_y materials.

BATT TASK 6

MODELING

TASK 6.1 - PI, INSTITUTION: John Newman, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Improved Electrochemical Models

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor transport properties, capacity, and power fade

OBJECTIVES: Develop experimental methods for measuring transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

GENERAL APPROACH: Use simulations to improve understanding of limitations in cell performance. Develop improved experimental methods for measuring transport and kinetic properties.

STATUS OCT 1, 2010: Experiments comparing the kinetics of different redox shuttles through passivating films on inert surfaces will be ongoing. Modeling the effects of impurities in lithium-ion batteries will be ongoing.

STATUS SEP 30, 2011: Experiments comparing the kinetics of ferrocene reduction through a passivating film will be complete. Experiments comparing the kinetics of different shuttles through passivating films on inert surfaces will be ongoing. Modeling long-term shape changes in lithium electrodes, including heat and pressure effects, will be ongoing. Modeling the effects of impurities in lithium-ion batteries will be ongoing.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles; 15-year calendar life

MILESTONES:

- (a) Develop mechanism for reduction of ferrocene through passivating film. (Oct. 11) **Complete**
- (b) Introduce heat effects into lithium shape-change model. (Jan. 11) **Canceled due to change in research direction.**
- (c) Incorporate stress and strain in ceramics and metals in shape-change model. (May 11) **Canceled due to change in research direction.**
- (d) Initiate rotating disk studies with different redox shuttles. (Aug. 11) **Canceled due to change in research direction.**
- (e) Incorporate stack pressure and anode protection layer in shape-change model. (Sep. 11) **Canceled due to change in research direction.**

PROGRESS TOWARD MILESTONES

Interaction of Redox Shuttles and the SEI

Previous quarterly reports presented both steady-state and impedance methods for characterizing through-film ferrocene reduction. An abstract on this subject was presented at the 220th Meeting of the Electrochemical Society, and a manuscript was submitted for publication. It was found that, although EIS does not provide as unique a fit as the steady-state measurements, the indicators of high-frequency arc width and time constant agree qualitatively with steady-state results. Impedance also has significant experimental advantages over the rotating disk electrode; it is faster, uses less material, and is less subject to variations in temperature and bulk concentration. Most importantly, it permits the use of more materials, including those actually found in Li-ion batteries. Previous work has found that the SEI formation reactions may differ substantially on the edge and basal planes of graphite; accordingly, the current task is to use the method developed in this work to study how passivation differs with graphite orientation. This project is taking place in collaboration with the research group of Professor Takeshi Abe at Kyoto University.

A preliminary result from this study is shown in Fig. 1. Two samples of HOPG, one with an edge fraction of 0.06 (primarily the basal surface exposed) and the other with an edge fraction of 0.6 (primarily the edge fraction exposed) were cycled from 3.7 to 0.1 V vs. Li/Li⁺ in a solution of 2 mM ferrocene in 1.0 M LiPF₆ in EC:DEC in order to form an SEI. The impedance spectra at open circuit were measured both before and after cycling. Figure 1 shows that, before SEI formation, impedance spectra on both samples exhibit a straight line of approximately 45° slope without any high-frequency semicircles (dashed lines).

The two dashed lines collapse because the kinetics are fast on both the edge and basal plane. After SEI formation, both samples show increased impedance, but the impedance on the edge plane is much higher than that on the basal plane, despite higher electronic activity on the edge plane. More work is required to confirm and explain the results shown in Fig. 1. However, these preliminary results demonstrate the ability of the developed method to characterize materials found in actual batteries. Future work will also compare behavior under different formation conditions and in different electrolytes.

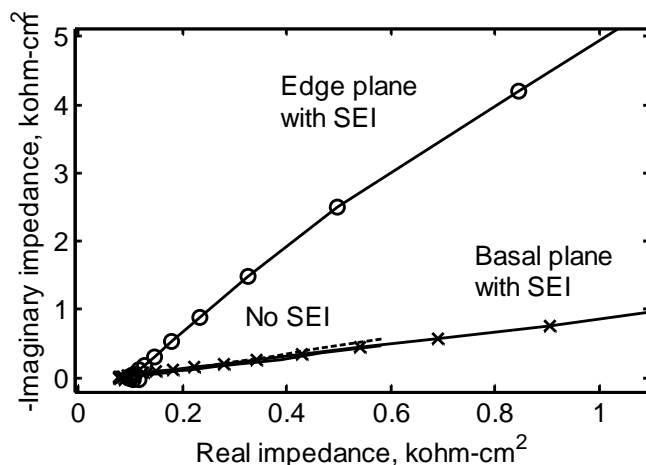


Figure 1. Comparison of through-film ferrocene impedance on the edge and basal planes of graphite.

TASK 6.2 - PI, INSTITUTION: Venkat Srinivasan, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Mathematical Modeling of Next-generation Li-ion Chemistries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy efficiency; low calendar/cycle life; high cost

OBJECTIVES:

1. Quantify the usefulness of alloy anodes for use in PHEVs.
2. Understand the mechanical degradation in electrodes used in EVs and PHEVs.
3. Model reaction distribution in battery electrodes.

GENERAL APPROACH: Develop mathematical models for candidate Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to connect fundamental material properties to performance and degradation modes and provide guidance to material-synthesis and cell-development PIs. Use models to quantify the ability of the candidate chemistry to meet DOE performance goals.

STATUS OCT. 1, 2010: The model development for silicon anode with a NMC cathode was completed. A 1-D model for LiFePO₄ that predicts the high rate capacity was completed. A model that accounts for mechanical stress in a single graphite particle was completed.

STATUS SEPT. 30, 2011: The performance models for Si anode with the NMC cathode will be complete and comparison made with the baseline. The degradation of graphite and candidate alloy anodes that takes into account the interaction of the active material and the binder will be complete. A model that accounts for the reaction distribution across the electrode will be developed and compared to experimental data.

RELEVANT USABC GOALS: *Available energy:* 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10-s discharge power:* 750 W/kg (10 mile) and 316 W/kg (40 mile).

MILESTONES:

- (a) Compare the performance of the Si/NMC system with the baseline high-energy system and quantify the improvements under PHEV conditions. (Jan. 11) **Complete**
- (b) Extend the mechanical degradation model developed for graphite anode to include volume change and pressure diffusion and report on the possible failure modes. (Mar. 11) **Complete**
- (c) Develop a 2D model for LiFePO₄ electrode, and compare the reaction distribution to experimental data. (Aug. 11) **On-giving, due Mar. 12**
- (d) Extend the silicon model to include the effect of mechanical stress and interaction of active material and binder and report on the effect of different binders on degradation. (Sep. 11) **On-going, due Feb. 12**

PROGRESS TOWARD MILESTONES

Over the previous quarter, the rate performance of the NMC cathode has been studied using thin electrodes (*ca.* 6 μm thick) in a half-cell configuration with a Li-metal counter electrode. Experimental results showed that the material is capable of fast charge and discharge and has good capacity retention. More than 50% of the capacity was still retained when discharging the electrodes at rates up to 100C. Even higher rate capability was seen for charge cycles and a clear asymmetry between the charge and discharge was observed.

In this quarter, the high rate capability of the NMC electrode was explored by examining the transport properties of the material at the particle scale. Porous electrode effects were minimized by the use of thin electrodes. This enabled the use of a continuum model of a single sphere to simulate the transport process in the particle. The diffusion of Li inside the NMC particle was assumed to be the limiting process of the intercalation reaction and was described by Fick's second law. The electrodes were set to open circuit after discharging to specific states of charge (SOC) in order to isolate the diffusion from other electrode processes. The diffusion coefficient of Li in the NMC particles was estimated qualitatively by matching the simulated and experimental potentials obtained during open-circuit relaxation.

The figure below shows the estimated Li diffusion coefficients at various SOC. The diffusion coefficient is strongly dependent on Li concentration. The increasing diffusion coefficient with increasing SOC also explains the asymmetry of electrode utilization between charge and discharge. The qualitative fitting result provides a basic description of the diffusion of Li in NMC particles with respect to SOC. Future work will examine how well the estimated Li diffusion coefficients can predict the potentials and capacities on the thin NMC electrodes. The results will then be carried forward to study thick, porous electrodes in order to examine the limitations due to the solution phase.

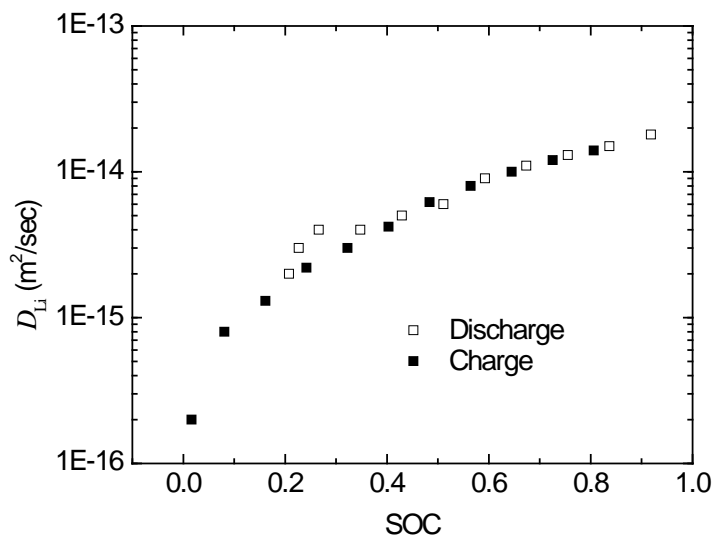


Figure 1. Estimated lithium diffusion coefficient as a function of state of charge. The charge data (■) was obtained by charging the electrode with several current interruptions, and the discharge data (□) was obtained by discharging the electrode with several current interruptions to estimate the diffusion coefficients at various states of charge.

TASK 6.3 - PI, INSTITUTION: Ann Marie Sastry, University of Michigan, Ann Arbor

TASK TITLE - PROJECT: Modeling – Thermo-electrochemistry, Capacity Degradation, and Mechanics with SEI Layer

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: Prediction of capacity degradation, and excessive conductive mass which penalizes energy and power density and increases cost.

OBJECTIVES: (i) multiscale finite element (FE) modeling considering self-assembly, its effect on cathode structure, and the effect in turn on cathode dissolution as the main effect in capacity degradation, (ii) parametric studies for SEI layer formation, (iii) validation of SEI layer formation model through *ex situ* and/or *in situ* experimental techniques

GENERAL APPROACH: Multiscale modeling of thermal electrochemistry will be extended with microstructure reconstruction *via* self assembly. The precipitation process including a nucleation phase and phase growth is governed by the interfacial energy differences between each species. By evaluating the parameters, we will explore the SEI growth phenomena. The formation and the structure of SEI layers are complex. SEI layers will be characterized and the SEI formation model will be validated by *exsitu* and/or *in situ* experimental techniques.

STATUS OCT. 1, 2010: Modeling of multiscale thermo-electrochemistry has allowed the inclusion of microstructural effects on the performance prediction of Li-ion batteries. SEI layer modeling including nucleation and growth processes has allowed the prediction of the multi-layered structure of SEI layers, which has been confirmed by many experiments. SEI layers formed on LiMn₂O₄ composite cathodes were characterized *ex situ* using IR (infrared) spectroscopy and/or Raman, SEM and TEM.

STATUS SEP. 30, 2011: We expect to extend/establish (1) multiscale FE model considering particle aggregation, its effect on cathode structure, and the effect in turn on cathode dissolution as the main effect in capacity degradation, (2) SEI layer formation model and parametric studies for different electrochemical systems, and (3) experimental techniques (using *ex situ* and/or *in situ*) to validate the SEI-layer formation model. Capacity degradation of Li-ion batteries can then be correlated to the properties of SEI layers and particle microstructures.

RELEVANT USABC GOALS: Available energy for CD mode: 3.4 kWh (10 miles) and 11.6 kWh (40 miles); Cycle life: 5000 cycles (10 miles) and 300,000 cycles (40 miles); 10- s discharge power: 45 kW (10 miles) and 38 kW (40 miles); Calendar life: 15 years (40°C).

MILESTONES

- (a) Implement multiscale modeling with self assembly and dissolution. (Mar. 11) **Complete**
- (b) Evaluate parameters such as interfacial energies. (May 11) **Complete**
- (c) Characterize microstructure and chemical elements of SEI layers. (Aug. 11) **Complete**

PROGRESS TOWARD MILESTONES

1) Multiscale modeling with self assembly and dissolution (Jul. 2011)

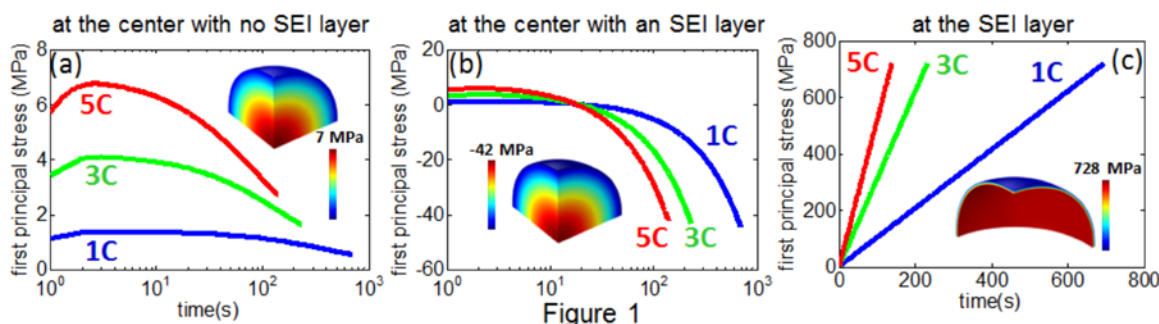
Effective material properties were measured by applying volume averaging theory to microstructure meshed with tetrahedral elements. Effective diffusivities and conductivities were compared *via* Bruggeman's equation, as seen in Table 1.

Table 1

	Volume fraction	Bruggeman(n=1.5)	3D microstructure
$D_{\text{active}}^{\text{eff}}/D_{\text{active}}$	0.49	0.34	0.346
$D_{\text{elyte}}^{\text{eff}}/D_{\text{elyte}}$	0.51	0.37	0.378
$\sigma_{\text{solid}}^{\text{eff}}/\sigma_{\text{solid}}$	0.49	0.34	0.300

2) Capacity fade due to SEI layer formation (Aug. 2011)

Anode particles near the separator underwent high stress due to (de)intercalation, which resulted in structural degradation of the active particles as shown in Fig. 1a. When the SEI layer was formed at the surface of the anode particle, this layer changed the stress evolution inside the particle due to the mismatch of the partial molar volume as shown in Fig. 1b. Also, this SEI layer itself underwent high stress due to the expansion of the active material inside as shown Fig.1c. This high stress may cause cracking and instability of the SEI layer that may reduce the battery performance.



3) Characterization of SEI layers (Sep. 2011)

Table 2 shows the change in element quantities for different temperatures from XPS measurements. The quantity of phosphorus was significantly increased as the temperature increased. This was due to greater decomposition of the LiPF_6 at high temperatures. Also, a relatively large amount of oxygen and Li was observed at high temperatures, indicating that more SEI layer components such as lithium alkyl carbonate, Li_2CO_3 , and LiF formed at high temperatures.

Table 2

Temperatures	Oxygen	Lithium	Phosphorus
0 °C	4.4 % increase	34.7% increase	20.4% increase
25 °C			
60 °C	19.4% increase	5.84% increase	109.2% increase

TASK 6.4 - PI, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling – Predicting and Understanding New Li-ion Materials Using *Ab Initio* Atomistic Computational Methods

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF₆+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High cost, low energy, low rate, poor cyclability.

OBJECTIVES: 1) Predict new chemistries and crystal structures for improved electrodes as defined by the goals of USABC. 2) Understand rate-limiting behavior in current electrode materials in order to target and design optimal diffusion properties in new materials.

GENERAL APPROACH: Use computational *ab initio* atomistic modeling methods to understand current Li-ion battery electrode materials and use this knowledge to suggest improvements as well as new electrode materials. Use statistical mechanics models to understand Li diffusion in bulk and on surfaces. Combine and make efficient access to all relevant calculated knowledge in a searchable database, which will greatly facilitate computational materials design.

STATUS OCT. 1, 2010: The analyses of Li diffusion in bulk graphite have been concluded. Evaluation of Al-substitution effect on LiNi_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO₂ in terms of Li mobility and electronic conductivity has been studied. Phase diagrams of several Li-Cu-M-O (M= polyanion metal) compounds have been analyzed and the necessary Cu-ion mobility has been bench marked.

STATUS SEP. 30, 2011: Comprehensive studies of surface morphology and Li diffusion on electrode material surfaces (graphite, Ni_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO₂ and LiFePO₄) will be underway. Investigation of surface band structure of LiFePO₄ with/without different surface absorbates will be finished. Conclusion for the Li-Cu-M-O project is expected.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; Operating charging temperature: - 30 to 52 °C

MILESTONES:

- (a) Calculate band structure of LiFePO₄ surfaces. (Dec. 10) **Complete**
- (b) Evaluate LiCoO₂ surface electronic structure. (Mar. 11) **Delayed, due Sep. 12**
- (c) Upload materials database. (May 11) **Complete**
- (d) Go/No-go decision on the Cu-Metal-O cathodes. (May 11) **Delayed, due Sep. 12**
- (e) Conclude preliminary evaluation of Li diffusion on LiCoO₂ and graphite surfaces. (Jun. 11) **Complete**

PROGRESS TOWARD MILESTONES

Collaborations: Prof Gerbrand Ceder (MIT), Dr. Jordi Cabana (LBNL), Dr Robert Kostecki (LBNL).

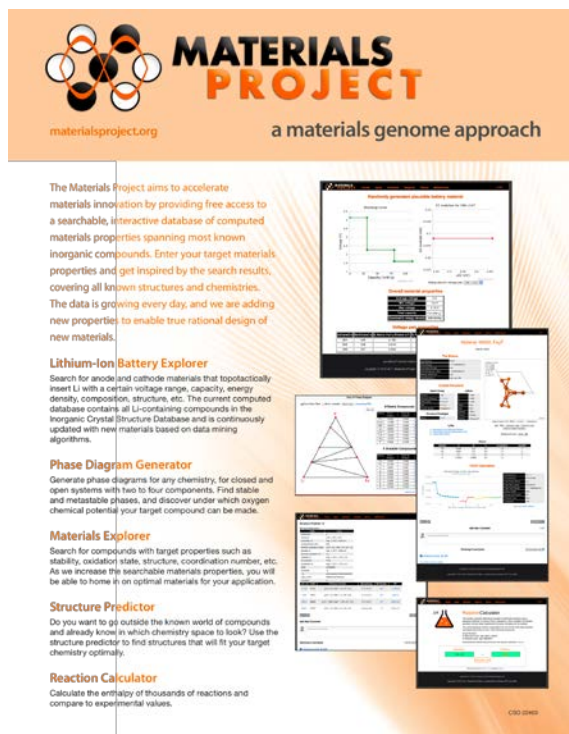


Figure 1. Announcement of the Materials Project www.materialsproject.org.

As part of the high-voltage spinel effort in the BATT group, the cation ordering influence on the stable ground states as a function of Li content in $\text{Li}_x(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$ has been investigated. Previous work has shown that the voltage profile is generally much more flat in the spinel where Ni (Mn) sits exclusively at 4b (12d) sites compared to the structure where both sites are occupied randomly by Ni or Mn. Our study unequivocally show how the preferred Li-Vac arrangement is incommensurate with the cation ordering in the ordered spinel, which results in an absence of intermediate Li concentration ground states. However, for uniformly disordered spinel the cation arrangement accommodates the preferred Li-Vac arrangement, which is exhibited in a strong ground state at half lithiated composition.

To conclude milestone (c) for 2011, the first Materials Project web site and database was successfully launched. The web site provides a gateway to free searchable access to general materials properties covering >15,000 inorganic compounds and the number of compounds increases continuously. The site contains tools ('apps') designed to aid in materials design for specific application areas such as Li-ion battery technology. Figure 1 shows the announcement featuring many of the possible search result capabilities of the web site – among them an example electrode material with its computed voltage profile and oxygen evolution as a function of charge. The Materials Project continues to compute more properties and materials – both known and unknown.

The effort on the LiCoO_2 surfaces has been delayed as the person designated for this research task was 10 months late arriving to LBNL due to visa issues. However, the researcher has now arrived and will shortly begin the study, which will be concluded within the next year.

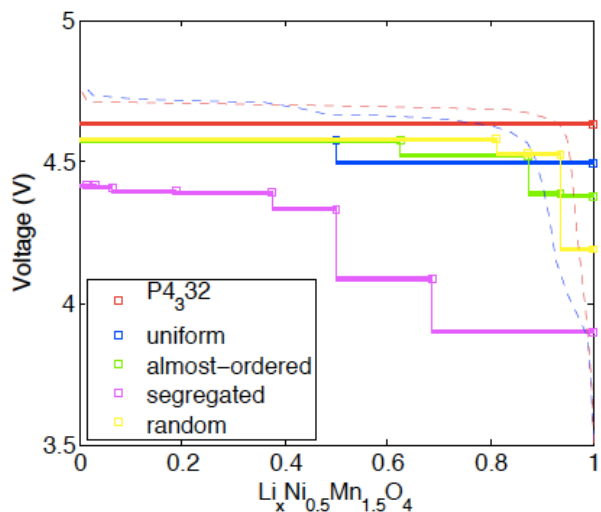


Figure 2. The voltage profiles for ordered (red) and 4 different disordered' (yellow, green, blue and magenta) versions of $\text{Li}_x(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$.